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(54) CYCLOOLEFINIC COPOLYMER, ITS COMPOSITE MATERIAL, THESE CROSSLINKED MATERIAL AND OPTICAL MATERIAL THEREFROM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cycloolefinic copolymer which is crosslinkable and capable of giving excellent properties in heat resistance, transparency, chemical resistance, solvent resistance, bonding and adhesion, its composite material, these crosslinked materials and optical materials using them.

SOLUTION: The cycloolefinic copolymer obtained by addition polymerization of a cycloolefin having specific crosslinkable functional groups and other cycloolefins, providing the weight average molecular weight of 3,000-1,500,000, the composite material prepared by compounding this copolymer with a specific metal oxide, these crosslinked materials and the optical materials using them are obtained.

Claim(s)]

[Claim 1] A cyclic olefin system copolymer whose polystyrene equivalent weight average molecular weights are 3,000-1,500,000 including a repeating unit (a) expressed with a following general formula (1), and a repeating unit (b) expressed with a following general formula (2).

[Formula 1]

Independently A^1 , A^2 , A^3 , and A^4 among [type (1), respectively A hydrogen atom, the hydrocarbon group of the carbon numbers 1-20, or, General formula-(CH₂)_f-O-C(O)CR¹=CR²R³ or general formula-C(O) the functional group which is expressed with -O-(CH₂)_g-O-C(O)-CR¹=CR²R³ and for which a bridge can be constructed. At least one of an example, A^1 , A^2 , A^3 , and A^4 is a functional group in which the above-mentioned bridge construction is possible. Here, R¹, R², and R³ show a hydrogen atom and the alkyl group of 1-10 independently, respectively. f shows the integer of 0-3 and g shows the integer of 1-3. p shows the integer of 0-3.]

[Formula 2]

B^1 , B^2 , B^3 , and B^4 among [type (2), respectively independently, A hydrogen atom, the alkyl group of the carbon numbers 1-20, a cycloalkyl group, an aryl group, an alkenyl group, a halogen atom, a halogenated hydrocarbon group, or the polar group expressed with -(CH₂)_qX is shown. X here -C(O)OR⁴, -OC(O)R⁵, Or it is -Si(OR⁶)_{3-k}R⁷_k. The alkyl group of the carbon numbers 1-20, an aryl group, cycloalkyl groups or these halogenation groups, and R⁶ of R⁴ and R⁵ are the alkyl groups, alkenyl groups, or aryl groups of the carbon numbers 1-10, R⁷ is a halogen atom, an alkyl group of the carbon numbers 1-10, an alkenyl group, or an allyl group. B^1 and B^3 may be BINIRIDENIRU, imide, and carboxylic anhydride groups which combine with each other and are formed. q shows the integer of 0-3. k is an integer of 0-3. m shows the integer of 0 or 1.]

[Claim 2] The cyclic olefin system copolymer according to claim 1 including a repeating unit (c) expressed with a following general formula (3).

- (CH₂-CHR⁸) - (3)

R⁸ is a silyl group expressed with a hydrogen atom, an alkyl group of the carbon numbers 1-8, an aryl group of the carbon numbers 6-15, or general formula-Si(R⁹)_t(R¹⁰)_{3-t} among [type (3). R⁹ shows an alkyl group or an alkoxy group of the carbon numbers 1-5 here, and R¹⁰ shows a halogen atom or a hydrogen atom. t is an integer of 0-3.]

[Claim 3]a repeating unit (a) shown by a general formula (1) -- the inside of all the repeating units -- 0.1 - 30-mol % -- the cyclic olefin system copolymer according to claim 1 or 2 contained.

[Claim 4]a repeating unit (b) whose at least one of B¹ of a general formula (2), B², B³, and B⁴ is alkoxy silyl groups -- the inside of all the repeating units -- 0.1 - 20-mol % -- the cyclic olefin system copolymer according to claim 1 or 2 contained.

[Claim 5]To claim 1 - a cyclic olefin system copolymer given in 4 any 1 paragraphs, silicon, A complex which blends a silicon oxide produced by carrying out hydrolysis condensation of an oxide of at least one sort of metal chosen from a group of aluminum, titanium, and a zirconium and/, or the alkoxy silane compound.

[Claim 6]A bridging body over which claim 1 - a cyclic olefin system copolymer given in 4 any 1 paragraphs, or the complex according to claim 5 was made to construct a bridge.

[Claim 7]An optical material using claim 1 - a cyclic olefin system copolymer given in 4 any 1 paragraphs, the complex according to claim 5, or the bridging body according to claim 6.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the cyclic olefin system copolymer which can construct a bridge. It is related with the suitable cyclic olefin system copolymer for the optical material which has the outstanding heat resistance, solvent resistance, and chemical resistance in more detail for which a bridge can be constructed, this complex, these bridging bodies, and the optical material using these.

[0002]

[Description of the Prior Art]In recent years, in fields, such as electronic parts and an optic, the conversion to transparent resin in which it is light and processing is easy from glass is progressing with the demand of a weight saving, and small size and densification. There are the strong points, like that it is easy to process it, that it can be hard to divide, and transparent resin as substitution of glass is light, and there is also a fault -- heat resistance, endurance and chemical resistance, and dimensional stability are inferior. Therefore, improving these faults is called for.

[0003]Transparency is optically made highly useful [the addition polymer of cyclic olefin] until now as an existing heat-resistant polymer, for example, the following patent is proposed.

JP,03-205408,A JP,04-63807,A JP,07-104474,A JP,09-508649,A JP,10-251343,A JP,10-182799,A WO -98/No. 20394 gazette WO-No. 97/20871 gazette WO-96/ The No. 37526 gazette WO-No. 98/56839 gazette [0004]In [it is supposed as an improvement means of heat

resistance, chemical resistance, and dimensional stability that it is bridge construction-ization a leading means, and] the following Patent Gazettes, The cyclic olefin system addition polymer which has an unsaturated bond of the hydrocarbon represented with (1) JP,03-205408,A with a vinyl group and a vinylidene group in a side chain as a cyclic olefin system polymer which can construct a bridge.

(2) The cyclic olefin system addition polymer which has a substituent which consists of a conjugate double bond which contains an aromatic group in the WO-No. 96/37526 gazette in a

side chain.

(3) The cyclic olefin system addition polymer which contains alkoxy silyl groups in a side chain as a representative in WO 98/No. 56839 gazette, WO 97/No. 20871 gazette, and WO 98/No. 20394 gazette. The cyclic olefin system polymer in which alkoxy silyl groups was introduced by the grafting reaction in JP,07-104474,A.

(4) The cyclic olefin system polymer by which epoxy denaturation was carried out in JP,10-182799,A and JP,10-251343,A. **** is indicated.

[0005]However, in the unsaturation bond groups which consists of hydrocarbon, such as a vinyl group as a reactive site which can construct a bridge, and a vinylidene group, in order to construct a bridge, many initiator compounds which are disassembled with heat, light, etc. and a radical generates are necessities. In the case of alkoxy silyl groups, the acid generator etc. which are disassembled with additive agents, such as water, acid, organic tin, and aluminum diketone, a catalyst, or light are required. In the use fields an optical material, for electronic industry materials, etc., things which are not included as much as possible in a polymer, such as a volatile impurity and a catalyst metal residue, are searched for. Therefore, even if the functional group as a reactive site which can construct a bridge works effectively and faces bridge construction, it is called for that a bridge is constructed by the method of not using these using the additive agent of the smallest possible quantity, a catalyst, etc.

[0006]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the cyclic olefin system copolymer which was made in view of the above-mentioned problem, and gives outstanding heat resistance, transparency, chemical resistance, solvent resistance, and adhesion and adhesion and for which a bridge can be constructed, its complex, and its bridging body. The cyclic olefin system copolymer over which the bridge was constructed aims at providing the impurity for bridge construction as much as possible, and the bridging body which does not contain a residue.

[0007]

[Means for Solving the Problem]This invention relates to a cyclic olefin system copolymer whose polystyrene equivalent weight average molecular weights are 3,000-1,500,000 including a repeating unit (a) expressed with a following general formula (1), and a repeating unit (b) expressed with a following general formula (2).

[0008]

[Formula 3]

[0009]Independently A^1 , A^2 , A^3 , and A^4 among [type (1), respectively A hydrogen atom, the hydrocarbon group of the carbon numbers 1-20, or, General formula-(CH₂)_r-O-C(O)CR¹=CR²R³ or general formula-C (O) the functional group which is expressed with -O-(CH₂)_g-O-C(O)-CR¹=CR²R³ and for which a bridge can be constructed. At least one of an example, A^1 , A^2 , A^3 , and A^4 is a functional group in which the above-mentioned bridge construction is possible. Here, R¹, R², and R³ show a hydrogen atom and the alkyl group of 1-10 independently,

respectively. f shows the integer of 0-3 and g shows the integer of 1-3. p shows the integer of 0-3.]

[0010]

[Formula 4]

[0011]B¹, B², B³, and B⁴ among [type (2), respectively independently, A hydrogen atom, the alkyl group of the carbon numbers 1-20, a cycloalkyl group, an aryl group, an alkenyl group, a halogen atom, a halogenated hydrocarbon group, or the polar group expressed with -(CH₂)_qX is shown. X here -C(O)OR⁴, -OC(O)R⁵, Or it is -Si(OR⁶)_{3-k}R⁷_k. The alkyl group of the carbon numbers 1-20, an aryl group, cycloalkyl groups or these halogenation groups, and R⁶ of R⁴ and R⁵ are the alkyl groups, alkenyl groups, or aryl groups of the carbon numbers 1-10, R⁷ is a halogen atom, an alkyl group of the carbon numbers 1-10, an alkenyl group, or an allyl group. It may be BINIRIDENIRU, imide, and carboxylic anhydride groups which are formed by B¹ and B³. q shows the integer of 0-3. k is an integer of 0-3. m shows the integer of 0 or 1.] Here, the above-mentioned cyclic olefin system copolymer may include the repeating unit (c) further expressed with a following general formula (3).

$-(CH_2-CHR^8)-\dots\dots (3)$

R⁸ is a silyl group expressed with a hydrogen atom, an alkyl group of the carbon numbers 1-8, an aryl group of the carbon numbers 6-15, or general formula-Si(R⁹)_t(R¹⁰)_{3-t} among [type (3). R⁹ shows an alkyl group or an alkoxy group of the carbon numbers 1-5 here, and R¹⁰ shows a halogen atom or a hydrogen atom. t is an integer of 0-3.] -- a repeating unit (a) shown again by a general formula (1) which constitutes the above-mentioned cyclic olefin system copolymer -- the inside of all the repeating units -- 0.1 - 30-mol % -- what is contained is preferred. a repeating unit (b) whose at least one of B¹ of a general formula (2) which constitutes the above-mentioned cyclic olefin system copolymer, B², B³, and B⁴ is alkoxy silyl groups -- the inside of all the repeating units -- 0.1 - 20-mol % -- what is contained is preferred. A silicon oxide produced by carrying out hydrolysis condensation of an oxide of at least one sort of metal chosen from a group of silicon, aluminum, titanium, and a zirconium and/, or the alkoxy silane compound is blended with a cyclic olefin system copolymer of this invention, and it is good for it also as a complex. Next, this invention relates to a bridging body over which make the above-mentioned cyclic olefin system copolymer or the above-mentioned complex come to construct a bridge. Next, this invention relates to an optical material which used the above-mentioned cyclic olefin system copolymer, the above-mentioned complex, or the above-mentioned bridging body.

[0012]

[Embodiment of the Invention]An embodiment of the invention is described concretely below. A cyclic olefin system copolymer including the repeating unit (b) shown in the repeating unit (a) which shows the cyclic olefin system copolymer of this invention in a general formula (1), and a general formula (2), Or it is a cyclic olefin system copolymer including the repeating unit (c) shown by the repeating unit (a) shown in a general formula (1), the repeating unit (b) shown in a general formula (2), and a general formula (3).

[0013]The repeating unit (a) shown by a general formula (1) can be formed by the addition condensation of the cyclic olefin (henceforth "specific cyclic olefin (1)") shown in a following general formula (4).

[0014]

[Formula 5]

[0015] A^1 , A^2 , A^3 , A^4 , and p are the same as what is shown in a formula (1) among [type (4).] the cyclic olefin system copolymer of this invention -- the rate of a repeating unit (a) -- 0.1 - 30-mol % -- if contained, bridge construction will become possible easily with light and heat. Storage stability comes to be inferior, when the rate becomes difficult to require bridge construction at less than 0.1% and exceeds 30-mol % on the other hand. The percentages of a repeating unit (a) are 0.5 - 10-mol % preferably.

[0016]A little 2 and 7 addition structural units other than 2 and 3 addition structural unit which were shown in a general formula (1) may be included in a repeating unit (a) of this invention.

[0017]As an example of specific cyclic olefin (1), Acrylic acid 2-(5-NORUBORUNENIRU) methyl (another name: ester of 2-hydroxymethyl-5-norbornene and acrylic acid), Acrylic acid 2-(3-methyl-5-NORUBORUNENIRU) methyl, acrylic acid 2-(3-ethyl-5-NORUBORUNENIRU) methyl, Methacrylic acid 2-(5-NORUBORUNENIRU) methyl, acrylic acid 2-(5-NORUBORUNENIRU) ethyl, Methacrylic acid 2-(5-NORUBORUNENIRU) ethyl, acrylic acid 5-NORUBORUNENIRU, Acrylic acid 2-methyl-5-NORUBORUNENIRU, methacrylic acid 5-NORUBORUNENIRU, Methacrylic acid 2-methyl-5-NORUBORUNENIRU, acrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7, and 10}] dodecenyl) methyl, Acrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl, methacrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl, Methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl, Acrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7, and 10}] dodecenyl), Acrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl), Methacrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl), methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) Crotonic acid 2-(5-NORUBONENIRU) methyl, crotonic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7, and 10}] dodecenyl), 2-hydroxyethyl acrylate and ester of 5-norbornene 2-carboxylic acid, 2-hydroxyethyl methacrylate and ester of 5-norbornene 2-carboxylic acid, 2-hydroxyethyl acrylate and ester of 2-methyl-5-norbornene 2-carboxylic acid, 2-hydroxyethyl methacrylate and ester of 2-methyl-5-norbornene 2-carboxylic acid, 2-hydroxypropyl acrylate and ester of 5-norbornene 2-carboxylic acid, Ester of 2-hydroxypropyl methacrylate and 5-norbornene 2-carboxylic acid, Ester of 2-hydroxypropyl acrylate, ester of 2-methyl-5-norbornene 2-carboxylic acid and 2-hydroxypropyl methacrylate, and 2-methyl-5-norbornene 2-carboxylic acid, etc. are mentioned.

[0018]A repeating unit (b) shown by a general formula (2) can be formed by addition condensation of cyclic olefin (henceforth "specific cyclic olefin (2)") shown in a following general formula (5).

[0019]

[Formula 6]

[0020]B¹, B², B³, B⁴, and m are the same as that of a formula (2) among [type (5).]

At least one of B¹ of the general formula (2) which constitutes the cyclic olefin system copolymer of this invention, B², B³, and B⁴ the repeating unit (b) which is alkoxy silyl groups, the inside of all the repeating units -- 0.1-20-mol % -- in order that what is contained may distribute the condensation product of a metallic oxide or an alkoxy silane compound micro and may consider it as the high complex of transparency optically, it is desirable in order to improve an adhesive property with other members. It is 0.5-10-mol % preferably.

[0021]As an example of specific cyclic olefin (2), 2-norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-propyl-2-norbornene, 5-butyl-2-norbornene, 5-pentyl-2-norbornene, 5-hexyl-2-norbornene, 5-heptyl-2-norbornene, 5-octyl-2-norbornene, 5-decyl-2-norbornene, 5-dodecyl-2-norbornene, 5,6-dimethyl-2-norbornene, 5-methyl-5-ethyl-2-norbornene, 5-phenyl-2-norbornene, 5-vinyl-2-norbornene, 5-allyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-ethylidene-2-norbornene, 5-cyclohexyl-2-norbornene, 5-cyclohexenyl 2-norbornene, 5-indenyl 2-norbornene, 5,6-Indang 2-norbornene, 5-fluoro-2-norbornene, 5-chloro-2-norbornene and 5-norbornene 2-methyl carboxylic acid, 5-norbornene 2-carboxylic acid ethyl, 5-norbornene 2-carboxylic acid butyl, 2-methyl-5-norbornene 2-methyl carboxylic acid, 2-methyl-5-norbornene 2-carboxylic acid ethyl, 2-methyl-5-norbornene 2-carboxylic acid propyl, 2-methyl-5-norbornene 2-carboxylic acid butyl, 2-methyl-5-norbornene 2-carboxylic acid trifluoroethyl, 2-methyl-5-norbornene 2-yl ethyl acetate, 5-trimethoxysilyl 2-norbornene, 5-dimethoxy chlorosilyl 2-norbornene, 5-methoxy chloromethyl silyl 2-norbornene, 5-dimethoxy chlorosilyl 2-norbornene, 5-methoxy hydride methylsilyl 2-norbornene, 5-dimethoxy hydride silyl 2-norbornene, 5-methoxy dimethylsilyl 2-norbornene, 5-triethoxy silyl 2-norbornene, 5-diethoxy chlorosilyl 2-norbornene, 5-ethoxy chloromethyl silyl 2-norbornene, 5-diethoxy hydride silyl 2-norbornene, 5-ethoxy dimethylsilyl 2-norbornene, 5-ethoxydiethylsilyl 2-norbornene, 5-propoxy dimethylsilyl 2-norbornene, 5-triphenoxy silyl 2-norbornene, 5-diphenoxymethylsilyl 2-norbornene, 5-trimethoxysilyl methyl-2-norbornene, 5-(2-trimethoxysilyl) ethyl-2-norbornene, 5-(2-dimethoxy, chlorosilyl) ethyl-2-norbornene, 5-(1-trimethoxysilyl) ethyl-2-norbornene, 5-(2-trimethoxysilyl) propyl-2-norbornene, 5-(1-trimethoxysilyl) propyl-2-norbornene, 5-triethoxy silyl ethyl-2-norbornene, 5-dimethoxymethylsilylmethyl-2-norbornene, 5-trimethoxy propylsilyl 2-norbornene, 5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 5-norbornene 2-carboxylic acid triethoxy silyl propyl, 5-norbornene 2-carboxylic acid dimethoxy, methylsilylpropyl, 2-methyl-5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 2-methyl-5-norbornene 2-carboxylic acid dimethoxy, methylpropyl, 2-methyl-5-norbornene 2-carboxylic acid triethoxy silyl propyl, 5-norbornene 2,3-dimethyl dicarboxylate, 5-norbornene 2,3-diethyl dicarboxylate, the 5-norbornene 2, 3-carboxylic anhydride, N-phenyl-5-norbornene 2,3-carvoneimide, N-cyclohexyl-5-norbornene 2,3-carvoneimide, 3-tricyclo [4.3.0.1^{2,5}] decene, 4.3.0.1^{2,3,7}-tricyclo [5] decadiene (dicyclopentadiene), 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecen, 4.4.0.1^{2,5}1^{7,8}-methyl-3-tetracyclo [10] dodecen, 8-methyl-8-carboxymethyl, 3-tetracyclo [4.4.0.1^{2,5}1^{7,10}] dodecen, 8-methyl-8-carboxyethyl, 4.4.0.1^{2,5}1^{7,3}-tetracyclo [10] dodecen, etc. can be mentioned.

[0022]A repeating unit (c) shown by a general formula (3) constituted with a repeating unit (b)

shown by repeating unit (a) shown by a general formula (1) and a general formula (2) is formed by carrying out addition copolymerization of "the specific alpha olefin."

[0023] As an example of specific alpha olefin, ethylene, propylene, 1-butene, 1-hexene, 1-octene, styrene, p-methylstyrene, o-methylstyrene, Although trimethylsilyl ethylene, triethyl silyl ethylene, trichlorosilyl ethylene, dimethyl chlorosilyl ethylene, methyldichlorosilylethylene, triethoxy silyl ethylene, tripropoxy silylethylene, etc. are mentioned, Ethylene, styrene, and p-methylstyrene are preferred in these.

[0024] A copolymerization method of a copolymerization method of specific cyclic olefin (1) of this invention and specific cyclic olefin (2) or cyclic olefin (1) and cyclic olefin (2), and specific alpha olefin is performed by a following method.

[0025] As a typical polymerization catalyst, $[\text{Pd}(\text{CH}_3\text{CN})_4]$ and $[\text{BF}_4]_2$, $[\text{Pd}(\text{PhCN})_4]$ $[\text{SbF}_6]$ di-mu-chloro-bis(6-methoxy bicyclo[2.2.1]hept 2-ene-, and sigma [5], 2pi)Pd (it abbreviates to "I" hereafter.), and methylalumoxane (it abbreviates to "MAO" hereafter.)

I, AgSbF_6 and I, AgBF_4 , $[(\text{eta}^3\text{-aryl})\text{PdCl}]_2$ and AgSbF_6 , $[(\text{eta}^3\text{-aryl})\text{PdCl}]_2$ and AgBF_4 , $[(\text{eta}^3\text{-clo chill})\text{Pd}(\text{cyclo-octadiene})]$, $[\text{PF}_6]$, $[(1, 5\text{-cyclo-octadiene})\text{Pd}(\text{CH}_3)(\text{Cl})]$, PPh_3 , $\text{NaB}[\text{3 and } 5\text{-(CF}_3)_2\text{C}_6\text{H}_3}]_4$ $[(\text{eta}^3\text{-clo chill})\text{nickel}(\text{cyclo-octadiene})]$, $[\text{B}(\text{CF}_3)_2(\text{C}_6\text{H}_4)]_4$

$[\text{NiBr}(\text{NPM}_2)_3]_4$, MAO, nickel(octate) $_2$ and MAO, nickel(octate) $_2$, $\text{B}(\text{C}_6\text{F}_5)_3$, and AlEt_3 , nickel(octate) $_2$, a reactant of HSbF_6 , BF_3 and Et_2O , and AlEt_3 , nickel. (Octoate) $_2$. A reactant of HSbF_6 . A reactant and AlEt_2F nickel of BF_3 and Et_2O , reactant nickel(octate) $_2$ of AlEt_3 , a reactant of HSbF_6 , $\text{AlEt}_2\text{FNi}(\text{octate})_2$, and HSbF_6 . (Naphthoate) Reactant nickel of $_2$, a reactant of HSbF_6 , BF_3 and Et_2O , $\text{AlBu}_3\text{nickel}(\text{naphthoate})_2$, a reactant of HSbF_6 , $\text{B}(\text{C}_6\text{F}_5)_3$, and AlEt_3 .

(Octoate) $_2$, $\text{Ph}_3\text{C-B}(\text{C}_6\text{F}_5)_3$, and AlEt_3 , Bis[N- (3-tert-butylsalicylidene) phenylaminato]nickel(II), $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, and $\text{AlBu}_3\text{Bis}[\text{N- (3-tert-butylsalicylidene) phenylaminato}]\text{nickel(II)}$ and MAO, nickel[PhC. (O) CHPh_2]. (Ph). (PPh_3) nickel[OC. (O) $(\text{C}_6\text{H}_4)\text{PPh}_2$](H) (PPh_3) nickel(COD) $_2$ and $\text{PPh}_3=\text{CHC}(\text{O})\text{Ph}[(\text{ArN}=\text{CHC}_6\text{H}_3(\text{O}) (\text{Anth}))]$

(Ph)(PPh_3) nickel (here)) Ar: 2, 6-(Pr) $_2\text{C}_6\text{H}_3$, Pr: isopropyl, Anth: 9-anthracene Toluene-nickel(C_6F_5) $_2$, $[\text{PPh}_2\text{CH}_2\text{C}(\text{O})\text{Ph}]$ nickel(C_6F_5) $_2$, A compound etc. which form a complex or cation complexes, such as nickel of periodic table 8 fellows, such as Co (neo decanoate) and MAO, Pd, and Co, are mentioned.

[0026] As a solvent, alicyclic hydrocarbon solvents, such as cyclohexane, cyclopentane, and methylcyclopentane, Aliphatic hydrocarbon solvents, such as pentane, hexane, heptane, and octane, Aromatic hydrocarbon solvents, such as toluene, benzene, and xylene, dichloromethane, Halogenated hydrocarbon solvents, such as 1,2-dichloroethylene and chlorobenzene, Ethyl acetate, butyl acetate, gamma-butyrolactone, propylene glycol, A solvent chosen from polar solvents, such as wood ether, nitromethane, N-methyl pyrrolidone, pyridine, N, N'-dimethylimidazolidinone, dimethylformamide, and an acetamide, etc. is used.

[0027] As the method of a polymerization, a monomer and a molecular weight modifier which become a reaction vessel from a solvent and cyclic olefin under nitrogen or argon atmosphere are taught, and a polymerization system is set as temperature of the range of -20°C - 100°C . Next, the above-mentioned catalyst component is added and it polymerizes in -20°C - 100°C . A weight ratio of a solvent/monomer is performed in 1-20. Regulation of a molecular weight is adjusted by the target molecular weight with an inversion rate and polymerization temperature to quantity of a polymerization catalyst, an addition of molecular weight modifiers, such as alpha olefin, hydrogen, and a diphenyl dihydrosilane, and a polymer. A stop of a polymerization is performed by compound chosen from water, alcohol, organic acid, carbon dioxide, etc. The water/alcoholic mixture of acid chosen as a polymer solution from organic carboxylic acid, such

as lactic acid and oxalic acid, are added, and a catalyst residue is separated and removed from a polymer solution. A polymer is obtained by putting a polymer solution in alcohol chosen from methanol, ethanol, isopropanol, etc., solidifying it, and carrying out reduced pressure drying. At this process, an unreacted monomer which remains in a polymer solution is also removed.

[0028] A molecular weight of a cyclic olefin system copolymer of this invention, o-dichlorobenzene. a number average molecular weight of polystyrene conversion measured by a gel permeation chromatography used as a solvent -- 2,000-1,000,000, and weight average molecular weight -- 3,000-1,500,000 -- desirable -- a number average molecular weight -- 10,000-700,000. Weight average molecular weight is 20,000-1,000,000. Disruptive strength when a number average molecular weight uses less than 2,000 and weight average molecular weight considers it as a film, a thin film, and a sheet by less than 3,000 becomes insufficient in many cases. On the other hand, if a number average molecular weight exceeds 1,000,000 and weight average molecular weight exceeds 1,500,000, the molding workability of a sheet and a film will fall, or solution viscosity will become high at the time of film production of a cast film, and handling will become difficult.

[0029] glass transition temperature of a cyclic olefin system copolymer of this invention is called for with peak temperature of temperature distribution of T_{δ} (a storage modulus -- E' -- a loss modulus -- E'' -- $Tan \delta = E'' / E'$) measured by dynamic viscoelasticity. 120-400 °C of glass transition temperature [200-370 °C of] of a cyclic olefin system copolymer of this invention is 250-350 °C especially preferably still more preferably. When glass transition temperature carries out liquid crystal group board formation in less than 120 °C at a film or a sheet shaped, heat resistance is insufficient, heat modification takes place, and it is not desirable. Since disassembly of a copolymer takes place on the other hand when performing processing in an elevated temperature, and crosslinking reaction, if glass transition temperature exceeds 400 °C, it is not desirable. A repeating unit (a) in a copolymer of this invention, For example, by an infrared absorption spectrum, can check by absorption of carbonyl (C=O) of a contiguity double bond of 1725-1735- cm^{-1} , etc., and with a nuclear magnetic resonance spectrum (1H -NMR). The structure can be checked from a peak of a proton of a carbon atom substituent of a 5.4-6.9 ppm C=C double bond. A rate of a repeating unit (a) in a copolymer can be searched for by 1H -NMR from a ratio of absorption of a 0.9-3.0 ppm proton, and absorption of a proton of a carbon atom substituent of a 5.4-6.9 ppm C=C double bond originating in all the norbornene structures.

[0030] In a cyclic olefin system copolymer of this invention, 2,6-di-tert-butyl-4-methylphenol, 4,4'-thiobis- (6-t-butyl-3-methyl phenol), 1,1'-bis(4-hydroxyphenyl)cyclohexane, 2,2'-methylenebis (4-ethyl-6-t-butylphenol), Phenol systems, such as 2,5-di-t-butylhydroquinone and pentaerythrityl tetrakis [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, To a hydroquinone system antioxidant pan, tris (4-methoxy-3,5-diphenyl) phosphite, Tris (nonylphenyl) phosphite, The Lynn system antioxidants, such as tris (2,4-di-t-butylphenyl) phosphite bis(2,6-di-t-butyl-4-methylphenyl)PENTAERI stole diphosphite bis(2,4-di-tert-butylphenyl) pentaerythritoldiphosphite, are added, Oxidation stability can be raised.

[0031] An oxide of at least one sort of metal chosen as a cyclic olefin system copolymer of this invention from a group of silicon, aluminum, titanium, and a zirconium, And a silicon oxide (these are also hereafter called "metallic oxide") produced by carrying out hydrolysis condensation of/or the alkoxy silane compound is blended, and it is good also as a complex.

[0032] As the above-mentioned complex, to a cyclic olefin system copolymer of above-mentioned this invention, the shape of colloidal one, It can also be considered as a complex

which mixed the surface with what denaturalized by acrylic ester which has alkoxy silyl groups for metallic oxides, such as silica, alumina, and a titania, or methacrylic acid ester, and a metallic oxide distributed micro in a copolymer and for which a bridge can be constructed.

[0033]A complex which a metallic oxide distributed micro in a copolymer and for which a bridge can be constructed is obtained without carrying out surface denaturation of the above-mentioned metallic oxide, when a cyclic olefin system copolymer of this invention contains alkoxy silyl groups.

[0034]furthermore -- as the above-mentioned complex -- the inside of a copolymer of this invention -- alcoholic salts, such as Si, aluminum, Ti, and Zr, and an aryl salt -- for example, A tetramethoxy silane, a tetraethoxysilane, methyl trimetoxysilane, methyl triethoxysilane, trimethoxy aluminum, and TORIE -- an ibis -- sial minium. By solution states, after mixing, catalysts, such as compounds, such as Sn, Ti, Zr, Y, and aluminum, and ** HCl and HF, are used, and a hybrid complex which can construct a bridge with hydrolysis and a "sol-gel method" which carries out a polycondensation is obtained in tetraethoxytitanium, tetraethoxy zircon, etc. When 100 nm or less of these inorganic particles are preferably distributed by particle diameter of 10 nm or less in a copolymer, it becomes the complex heat resistance and whose dimensional stability improved by optical transparency.

[0035]In a complex of this invention, loadings of the above-mentioned metallic oxide are usually five to 30 weight section preferably three to 50 weight section to cyclic olefin system copolymer 100 weight section of this invention.

[0036]A cyclic olefin system copolymer (or complex) of this invention, With an extruder, directly, can also consider it as a film and a sheet thin film, and, dissolve a copolymer (complex) in a solvent chosen from polar solvents, such as a hydrocarbon solvent, a halogenated hydrocarbon solvent, ketone, ether, ester, amine, amide, and urea, and pass casting and an evaporation process -- optics -- it can be made a transparent film and a sheet. A copolymer (complex) can also be fabricated and processed at a film and a sheet, evaporating a solvent with an extruder, after swelling a copolymer (complex) to these solvents.

[0037]A cyclic olefin system copolymer of this invention, Or in order for the complex to be able to construct a bridge with activity energy lines, such as light or an electron beam, and to promote bridge construction, Sensitizers, such as aromatic compounds, an aromatic carbonyl compound, and aromatic thiocarbonyl compounds, an organic and inorganic peroxide, a sulfide compound, a diazo compound, thiol compounds, etc. can be added in small quantities. As a light source used for bridge construction, light whose wavelength is 250 nm - 450 nm is used. Temperature is 0-150 ** and time of a cross-linking condition is 1 to 300 minutes.

[0038]A cyclic olefin system copolymer of this invention, its complex, and these bridging bodies, since it has outstanding optical transparency, heat resistance, and adhesion and adhesion - - optics (optical material), such as a light guide plate, a polarization film, a liquid crystal panel, a phase difference film, a transparent conductive film, an OHP film, an optical disc, an optical fiber, and a lens, and electronic parts -- it is further used for a medical care container, a container, etc.

[0039]A cyclic olefin system copolymer (complex) of this invention, Since it has outstanding optical transparency, heat resistance, an adhesive property, and adhesion, a hydride and an addition (**) polymer of a conventionally publicly known norbornene system ring breakage (**) polymer. for example, JP,61-29260,A and JP,60-16870,A, JP,60-26024,A, JP,2-51511,A, JP,1-132625,A, JP,1-132626,A, JP,4-202404,A, JP,4-63807,A, JP,8-198919,A, the Patent Publication Heisei No. 508649 [nine to] gazette, the Patent Publication Heisei No. 505880 [11 to] gazette,

JP,61-292601,A etc. can be blended and a thermoplastic polymer composition, nothing, outstanding heat resistance, an optical property (transparency, low birefringence), and adhesion and adhesion can be given.

[0040]In such a thermoplastic polymer composition, although a blending ratio of a cyclic olefin system copolymer of this invention and other polymers (**) is suitably chosen according to a kind of a cyclic olefin system copolymer of this invention, and other polymers (**), both compatibility, and the purpose of using a constituent, In order to obtain a polymer composition which has the outstanding heat resistance, a rate of a cyclic olefin system copolymer of this invention is 20 to 80 % of the weight still more preferably ten to 90% of the weight preferably five to 95% of the weight.

[0041]Such a thermoplastic polymer composition is obtained mechanical mixing which uses an extruder, a Banbury mixer, a kneader, a roll mill, etc., and by melting in a solvent and carrying out a solution blend. A film, a sheet, and a thin film can be obtained from such a thermoplastic polymer composition as well as a case of a cyclic olefin system copolymer of this invention.

[0042]

[Example]Hereafter, although an example explains this invention still more concretely, this invention does not receive restriction at all according to these examples. A molecular weight, glass transition temperature, a refractive index, glass transition temperature, a coefficient of linear expansion, water absorption, and adhesion and adhesion were measured by the following method.

[0043](1) Weight average molecular weight, a number average molecular weight : it measured at 120 ** by using o-dichlorobenzene as a solvent using H type column by TOSOH CORP. with the product 150C type gel-permeation-chromatography (GPC) device made by UOTAZU (WATERS). The obtained molecular weight is a standard polystyrene reduced property.

(2) Total light transmittance : based on ASTM-D1003, the 100-micrometer-thick film was used and total light transmittance was measured.

(3) Peak temperature of T δ (glass transition temperature) : T δ (ratio E'/E''=T δ of storage-modulus E' and loss-modulus E'') of dynamic viscoelasticity was measured, and peak temperature of the temperature distribution was made into the glass transition temperature of a copolymer. The test frequency performed measurement of dynamic viscoelasticity using LEO Vibron DDV-01FP (product made from a cage ene tech) on the conditions whose single waveform and excitation amplitude is 10 Hz and a part for /and whose 4 ** excitation modes a heating rate is 2.5 micrometers.

Coefficient of linear expansion : (4) TMA (Thermal Mechanical Analysis) / SS6100 (made by the SEIKO instrument company) are used, After having fixed in the distance between zippers of 10 mm, once carrying out temperature up of the sample 100 micrometers of thickness, 3 mm in width, and 10 cm in length from a room temperature to about 200 ** and taking a residual strain, temperature up was carried out by 3 ** / min. from the room temperature, and the coefficient of linear expansion was calculated from the elongation of the distance between zippers.

(5) Water absorption : after making it immersed in underwater [23 **] for 24 hours, water absorption was searched for from the weight change before and behind immersion.

An adhesive property and adhesion : (6) Vapor-deposit aluminum to a specimen (10 cm x 10 cm), and to this vacuum evaporation film by a cutter. The squares (1 mm x 1 mm) put in slitting, did the friction test by a cellophane tape, and measured ten pieces x the ten number of the blocks in 25 blocks which exfoliated so that it might be formed.

[0044]The synthetic example 1 [Composition of acrylic acid 2-(5-NORUBORUNENIRU)

methyl]

50 g (0.403 mol) of 5-hydroxymethyl-2-norbornene and 39.2 ml (0.483 mol) of acrylic acid chloride are added to 370 ml of methylene chlorides in a 500-ml resisting pressure container and under a nitrogen atmosphere, Furthermore, it is triethylamine. 84.3 ml (0.605 mol) was added and it was made to react at 25 °C for 3 hours. Then, it flowed into the hydrochloric acid aqueous solution, the aqueous phase was neutralized by sodium carbonate, and the organic phase was separated by the separating funnel. 75 mg of pentaerythrityl tetrakis [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] which is polymerization inhibitor was added, and it distilled under 55 °C and 5mmHg. 47 g was obtained for acrylic acid 2-(5-NORUBONENIRU) methyl. (65% of yield)

[0045]Example 1 [Composition of the copolymer of 2-norbornene and acrylic acid 2-(5-NORUBORUNENIRU) methyl]

Toluene with a moisture of 5 ppm under a nitrogen atmosphere to a 300-ml pressure bottle 100 ml, 2-norbornene 90mmol. and acrylic acid 2-(5-NORUBORUNENIRU) methyl 10mmol. are taught, Antimony hexafluoride acid (HSbF₆) and octanoic acid nickel (nickel(oct)₂) at -30 °C beforehand, The denaturation octanoic acid nickel (HSbF₆/nickel(oct)₂=1.2 mole ratio) made to react 0.04 mg-equivalent nickel, It added in order of trifluoride boron and ethyl ether complex 0.36mmol. triethylaluminum 0.40mmol., and the polymerization was performed at 30 °C for 2 hours. After adding to the above-mentioned copolymer solution and making 4 ml of isopropanols [60 °C of] containing lactic acid 4mmol. react to it for 30 minutes, it put into 600 ml of water, and it stirred, and settlement separation was carried out and the decatalyst was performed from the copolymer solution. Then, the copolymer solution was put into 1,000 ml of isopropanol, and was solidified, the unreacted monomer was removed, 80 °C of copolymers were dried for 10 hours, and the white powder 4.7g was obtained. The inversion rate to the copolymer of a monomer was 46%.

[0046]Analysis of a copolymer : - The CH₂= proton 5.4 of the CH₂=CH-CO-O-substituent originating in the 0.9-3.0 ppm proton peak and acrylic acid 2-(5-NORUBORUNENIRU) methyl originating in the norbornene structure measured by the presentation of 270 MHz of a copolymer, and ¹H-NMR. - the percentage of the structural unit which originates in acrylic acid 2-(5-NORUBORUNENIRU) methyl from 6.5 ppm was 3.2-mol %. The 5.0-5.3 ppm proton of the -CH=CH-structure generated by the ring opening polymerization of norbornene structure was not observed. The ¹H-NMR chart of the obtained copolymer is shown in drawing 1.

- Qualitative analysis of a functional group : the characteristic absorption of the ester group of 1,727-cm⁻¹ by CH₂=CH-CO-O- and the characteristic absorption of 1,636-cm⁻¹ by C=C were observed with the infrared absorption spectrum. The infrared absorption spectrum of the obtained copolymer is shown in drawing 2.

- Molecular weight : the number average molecular weight of the standard polystyrene conversion measured by GPC was 108,000, and weight average molecular weight was 233,000.

- Glass transition temperature : the peak temperature (glass transition temperature) of temperature distribution of T_{delta} was 350 °C.

- Total light transmittance : the total light transmittance measured using a 100-micrometer-thick film was 91%.

[0047]The with a crosslinking treatment [100-micrometer thickness unconstructed a bridge] cast film dissolved in toluene at 25 °C. When the high-pressure mercury lamp of 500W was used for this film and the main peak of wavelength irradiated with 314, 366, and the ultraviolet rays that are 405 or 436 nm at 30 °C via the heat ray cut-off filter for 30 minutes, the film became

insoluble to 25 ** toluene.

[0048] Instead of example 2 acrylic-acid 2-(5-NORUBONENIRU) methyl, it polymerized like Example 1 except using methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl) methyl. The inversion rate to the copolymer of a monomer was 82%. The percentage of the structural unit originating in methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl) methyl in a copolymer was 9.5-mol% from ¹H-NMR analysis. The number average molecular weight by GPC was 113,000, and weight average molecular weight was 226,000. By the exposure of ultraviolet rays, it became 25 ** toluene with the completely insoluble film like Example 1. When 90 ** of films which obtained benzoyl peroxide by carrying out 0.5 weight-section addition per polymer 100 weight section were heat-treated for 15 minutes, it became 25 ** and toluene with the completely insoluble film.

[0049] Instead of example 3 methacrylic-acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl) methyl 10mmol, Except using methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl) methyl 5mmol and 5-triethoxy silyl 2-norbornene 5mmol, it polymerized like Example 1 and the copolymer 7.3g was obtained. Methacrylic acid 3 - (the percentage of the structural unit originating in 8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl methyl was 4.8-mol % from ¹H-NMR analysis.) The rate of the structural unit originating in 5-triethoxy silyl 2-norbornene, It asked by infrared analysis from the analytical curve of the relative ratio of absorption of end CH₃ of the -Si-0-CH₂CH₃ group of 1,389-cm⁻¹, and absorption of -CH- by the norbornene skeleton of 1,294-cm⁻¹, and was 4.5-mol %. The number average molecular weight of this copolymer was 109,000, and weight average molecular weight was 214,000. A 100-micrometer film was created like Example 1, and bridge construction by ultraviolet rays was performed. It was completely insoluble to 25 ** toluene in the film. The total light transmittance of this film was 91%. There was no block with which the peel test of aluminum also exfoliates.

[0050] It is a silica particle (the mean particle diameter of 12 nm) in 400 ml of example 4 methyl ethyl ketone. Specific surface area ² of 400 m, surface silanol 5micromol/m², Or 50 g of meta-cloxy (propyl) trimethoxysilane is added for an alumina particle (mean particle diameter of 20 nm, specific surface area ² of 150 m) to 100 g, respectively, Furthermore, a 1.5-g maleic anhydride was added to 10 ml of water as a catalyst, and it returned under nitrogen for 2 hours. 200 ml was removed from this solution under decompression of methyl ethyl ketone, and 200 ml of toluene was added. Thus, five weight sections were mixed for obtained colloidal silica or alumina of surface denaturation in the toluene solution to copolymer 100 weight of Example 3, and the composite-ized transparent solution was obtained. Next, the cast of the solution was carried out and about 100-micrometer film was obtained. The weighted solidity of the composite-ized film and the film which carried out optical bridge construction is shown in Table 1.

[0051]

[Table 1]

[0052]In example 5 Example 1, it carried out like Example 1 instead of acrylic acid 2-(5-NORUBORUNENIRU) methyl except using 2-hydroxyethyl methacrylic acid ester and ester of 2-methyl and 5-norbornene 2-carboxylic acid. The inversion rate to the polymer was 38%. The polymer was dissolved with toluene and the characteristic absorption of $1,727\text{-cm}^{-1}$ by $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-$ was observed in the infrared absorption spectrum after acetone solidifies and refines. The percentage of the structural unit originating in this structure was 2.8-mol % among all the repeating units. The number average molecular weight of the polymer was 39,000, and weight average molecular weight was 66,000. Like Example 1, the bridge construction by light took place and it was insoluble to toluene.

[0053]In comparative example 1 Example 1, instead of 2-norbornene 90mmol and acrylic acid 2-(5-NORUBORUNENIRU) methyl 10mmol, Using 2-norbornene 93mmol and 5-ethylidene-2-norbornene 7mmol, except using cyclohexane as a solvent, the copolymerization reaction was performed like Example 1 and the copolymer 7.6g was obtained. The number average molecular weight by GPC was 98,000, and weight average molecular weight was 198,000. Although a 100-micrometer film was created like Example 1 and the film was irradiated with ultraviolet rays, it mostly dissolved in cyclohexane. The remaining thing did not retain the original form with pastiness, either. Although benzoyl peroxide was added like Example 2 and the film was created and heated, it dissolved in cyclohexane. When the peel test of aluminum was carried out, it exfoliated altogether and adhesion was remarkably weak.

[0054]

[Effect of the Invention]According to this invention, the cyclic olefin system copolymer which can give outstanding heat resistance, transparency, chemical resistance, solvent resistance, and adhesion and adhesion and for which a bridge can be constructed, its complex, and also these bridging bodies can be provided.

TECHNICAL FIELD

[Field of the Invention]This invention relates to the cyclic olefin system copolymer which can construct a bridge. It is related with the suitable cyclic olefin system copolymer for the optical material which has the outstanding heat resistance, solvent resistance, and chemical resistance in more detail for which a bridge can be constructed, this complex, these bridging bodies, and the optical material using these.

PRIOR ART

[Description of the Prior Art]In recent years, in fields, such as electronic parts and an optic, the conversion to transparent resin in which it is light and processing is easy from glass is progressing with the demand of a weight saving, and small size and densification. There are the strong points, like that it is easy to process it, that it can be hard to divide, and transparent resin as substitution of glass is light, and there is also a fault -- heat resistance, endurance and chemical resistance, and dimensional stability are inferior. Therefore, improving these faults is called for.

[0003]Transparency is optically made highly useful [the addition polymer of cyclic olefin] until now as an existing heat-resistant polymer, for example, the following patent is proposed.

JP,03-205408,A JP,04-63807,A JP,07-104474,A JP,09-508649,A JP,10-251343,A JP,10-182799,A WO -98/No. 20394 gazette WO-No. 97/20871 gazette WO-96/. The No. 37526 gazette WO-No. 98/56839 gazette [0004]In [it is supposed as an improvement means of heat

resistance, chemical resistance, and dimensional stability that it is bridge construction-ization a leading means, and] the following Patent Gazettes, The cyclic olefin system addition polymer which has an unsaturated bond of the hydrocarbon represented with (1) JP,03-205408,A with a vinyl group and a vinylidene group in a side chain as a cyclic olefin system polymer which can construct a bridge.

(2) The cyclic olefin system addition polymer which has a substituent which consists of a conjugate double bond which contains an aromatic group in the WO-No. 96/37526 gazette in a side chain.

(3) The cyclic olefin system addition polymer which contains alkoxy silyl groups in a side chain as a representative in WO 98/No. 56839 gazette, WO 97/No. 20871 gazette, and WO 98/No. 20394 gazette. The cyclic olefin system polymer in which alkoxy silyl groups was introduced by the grafting reaction in JP,07-104474,A.

(4) The cyclic olefin system polymer by which epoxy denaturation was carried out in JP,10-182799,A and JP,10-251343,A. **** is indicated.

[0005]However, in the unsaturation bond groups which consists of hydrocarbon, such as a vinyl group as a reactive site which can construct a bridge, and a vinylidene group, in order to construct a bridge, many initiator compounds which are disassembled with heat, light, etc. and a radical generates are necessities. In the case of alkoxy silyl groups, the acid generator etc. which are disassembled with additive agents, such as water, acid, organic tin, and aluminum diketone, a catalyst, or light are required. In the use fields an optical material, for electronic industry materials, etc., things which are not included as much as possible in a polymer, such as a volatile impurity and a catalyst metal residue, are searched for. Therefore, even if the functional group as a reactive site which can construct a bridge works effectively and faces bridge construction, it is called for that a bridge is constructed by the method of not using these using the additive agent of the smallest possible quantity, a catalyst, etc.

EFFECT OF THE INVENTION

[Effect of the Invention]According to this invention, the cyclic olefin system copolymer which can give outstanding heat resistance, transparency, chemical resistance, solvent resistance, and adhesion and adhesion and for which a bridge can be constructed, its complex, and also these bridging bodies can be provided.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the cyclic olefin system copolymer which was made in view of the above-mentioned problem, and gives outstanding heat resistance, transparency, chemical resistance, solvent resistance, and adhesion and adhesion and for which a bridge can be constructed, its complex, and its bridging body. The cyclic olefin system copolymer over which the bridge was constructed aims at providing the impurity for bridge construction as much as possible, and the bridging body which does not contain a residue.

MEANS

[Means for Solving the Problem]This invention relates to a cyclic olefin system copolymer whose polystyrene equivalent weight average molecular weights are 3,000-1,500,000 including a repeating unit (a) expressed with a following general formula (1), and a repeating unit (b) expressed with a following general formula (2).

[0008]

[Formula 3]

[0009]Independently A^1 , A^2 , A^3 , and A^4 among [type (1), respectively A hydrogen atom, the hydrocarbon group of the carbon numbers 1-20, or, General formula-(CH₂)_f-O-C(O)CR¹=CR²R³ or general formula-C (O) the functional group which is expressed with -O-(CH₂)_g-O-C(O)-CR¹=CR²R³ and for which a bridge can be constructed. At least one of an example, A^1 , A^2 , A^3 , and A^4 is a functional group in which the above-mentioned bridge construction is possible. Here, R¹, R², and R³ show a hydrogen atom and the alkyl group of 1-10 independently, respectively. f shows the integer of 0-3 and g shows the integer of 1-3. p shows the integer of 0-3.]

[0010]

[Formula 4]

[0011] B^1 , B^2 , B^3 , and B^4 among [type (2), respectively independently, A hydrogen atom, the alkyl group of the carbon numbers 1-20, a cycloalkyl group, an aryl group, an alkenyl group, a halogen atom, a halogenated hydrocarbon group, or the polar group expressed with -(CH₂)_qX is shown. X here -C(O)OR⁴, -OC(O)R⁵, Or it is -Si(OR⁶)_{3-k}R⁷_k, The alkyl group of the carbon

numbers 1-20, an aryl group, cycloalkyl groups or these halogenation groups, and R^6 of R^4 and R^5 are the alkyl groups, alkenyl groups, or aryl groups of the carbon numbers 1-10, R^7 is a halogen atom, an alkyl group of the carbon numbers 1-10, an alkenyl group, or an allyl group. It may be BINIRIDENIRU, imide, and carboxylic anhydride groups which are formed by B^1 and B^3 . q shows the integer of 0-3. k is an integer of 0-3. m shows the integer of 0 or 1.] Here, the above-mentioned cyclic olefin system copolymer may include the repeating unit (c) further expressed with a following general formula (3).

$-(CH_2-CHR^8)-\dots\dots (3)$

R^8 is a silyl group expressed with a hydrogen atom, an alkyl group of the carbon numbers 1-8, an aryl group of the carbon numbers 6-15, or general formula- $Si(R^9)_t(R^{10})_{3-t}$ among [type (3)]. R^9 shows an alkyl group or an alkoxy group of the carbon numbers 1-5 here, and R^{10} shows a halogen atom or a hydrogen atom. t is an integer of 0-3.] -- a repeating unit (a) shown again by a general formula (1) which constitutes the above-mentioned cyclic olefin system copolymer -- the inside of all the repeating units -- 0.1 - 30-mol % -- what is contained is preferred. a repeating unit (b) whose at least one of B^1 of a general formula (2) which constitutes the above-mentioned cyclic olefin system copolymer, B^2 , B^3 , and B^4 is alkoxy silyl groups -- the inside of all the repeating units -- 0.1 - 20-mol % -- what is contained is preferred. A silicon oxide produced by carrying out hydrolysis condensation of an oxide of at least one sort of metal chosen from a group of silicon, aluminum, titanium, and a zirconium and/, or the alkoxy silane compound is blended with a cyclic olefin system copolymer of this invention, and it is good for it also as a complex. Next, this invention relates to a bridging body over which make the above-mentioned cyclic olefin system copolymer or the above-mentioned complex come to construct a bridge. Next, this invention relates to an optical material which used the above-mentioned cyclic olefin system copolymer, the above-mentioned complex, or the above-mentioned bridging body.

[0012]

[Embodiment of the Invention]An embodiment of the invention is described concretely below. A cyclic olefin system copolymer including the repeating unit (b) shown in the repeating unit (a) which shows the cyclic olefin system copolymer of this invention in a general formula (1), and a general formula (2), Or it is a cyclic olefin system copolymer including the repeating unit (c) shown by the repeating unit (a) shown in a general formula (1), the repeating unit (b) shown in a general formula (2), and a general formula (3).

[0013]The repeating unit (a) shown by a general formula (1) can be formed by the addition condensation of the cyclic olefin (henceforth "specific cyclic olefin (1)") shown in a following general formula (4).

[0014]

[Formula 5]

[0015] A^1 , A^2 , A^3 , A^4 , and p are the same as what is shown in a formula (1) among [type (4)]. the cyclic olefin system copolymer of this invention -- the rate of a repeating unit (a) -- 0.1 - 30-mol % -- if contained, bridge construction will become possible easily with light and heat. Storage stability comes to be inferior, when the rate becomes difficult to require bridge

construction at less than 0.1% and exceeds 30-mol % on the other hand. The percentages of a repeating unit (a) are 0.5 - 10-mol % preferably.

[0016] A little 2 and 7 addition structural units other than 2 and 3 addition structural unit which were shown in a general formula (1) may be included in a repeating unit (a) of this invention.

[0017] As an example of specific cyclic olefin (1), Acrylic acid 2-(5-NORUBORUNENIRU) methyl (another name: ester of 2-hydroxymethyl-5-norbornene and acrylic acid), Acrylic acid 2-(3-methyl-5-NORUBORUNENIRU) methyl, acrylic acid 2-(3-ethyl-5-NORUBORUNENIRU) methyl, Methacrylic acid 2-(5-NORUBORUNENIRU) methyl, acrylic acid 2-(5-NORUBORUNENIRU) ethyl, Methacrylic acid 2-(5-NORUBORUNENIRU) ethyl, acrylic acid 5-NORUBORUNENIRU, Acrylic acid 2-methyl-5-NORUBORUNENIRU, methacrylic acid 5-NORUBORUNENIRU, Methacrylic acid 2-methyl-5-NORUBORUNENIRU, acrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7, and 10}] dodecenyl) methyl, Acrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methylmethacrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl, Methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl, Acrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7, and 10}] dodecenyl), Acrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl), Methacrylic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl), methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl)

Crotonic acid 2-(5-NORUBONENIRU) methyl, crotonic acid 3-(3-methyl-8-tetracyclo [4.4.0.1^{2,5}.1^{7, and 10}] dodecenyl), 2-hydroxyethyl acrylate and ester of 5-norbornene 2-carboxylic acid, 2-hydroxyethyl methacrylate and ester of 5-norbornene 2-carboxylic acid, 2-hydroxyethyl acrylate and ester of 2-methyl-5-norbornene 2-carboxylic acid, 2-hydroxyethyl methacrylate and ester of 2-methyl-5-norbornene 2-carboxylic acid, 2-hydroxypropyl acrylate and ester of 5-norbornene 2-carboxylic acid, Ester of 2-hydroxypropyl methacrylate and 5-norbornene 2-carboxylic acid, Ester of 2-hydroxypropyl acrylate, ester of 2-methyl-5-norbornene 2-carboxylic acid and 2-hydroxypropyl methacrylate, and 2-methyl-5-norbornene 2-carboxylic acid, etc. are mentioned.

[0018] A repeating unit (b) shown by a general formula (2) can be formed by addition condensation of cyclic olefin (henceforth "specific cyclic olefin (2)") shown in a following general formula (5).

[0019]

[Formula 6]

[0020] B¹, B², B³, B⁴, and m are the same as that of a formula (2) among [type (5).]

At least one of B¹ of the general formula (2) which constitutes the cyclic olefin system copolymer of this invention, B², B³, and B⁴ the repeating unit (b) which is alkoxy silyl groups, the inside of all the repeating units -- 0.1-20-mol % -- in order that what is contained may distribute the condensation product of a metallic oxide or an alkoxy silane compound micro and may consider it as the high complex of transparency optically, it is desirable in order to improve an adhesive property with other members. It is 0.5-10-mol % preferably.

[0021] As an example of specific cyclic olefin (2), 2-norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-propyl-2-norbornene, 5-butyl-2-norbornene, 5-pentyl-2-norbornene, 5-hexyl-2-norbornene, 5-heptyl-2-norbornene, 5-octyl-2-norbornene, 5-decyl-2-norbornene, 5-

dodecyl-2-norbornene, 5,6-dimethyl-2-norbornene, 5-methyl-5-ethyl-2-norbornene, 5-phenyl-2-norbornene, 5-vinyl-2-norbornene, 5-allyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-ethylidene-2-norbornene, 5-cyclohexyl-2-norbornene, 5-cyclohexenyl 2-norbornene, 5-indenyl 2-norbornene, 5,6-Indang 2-norbornene, 5-fluoro-2-norbornene, 5-chloro-2-norbornene and 5-norbornene 2-methyl carboxylic acid, 5-norbornene 2-carboxylic acid ethyl, 5-norbornene 2-carboxylic acid butyl, 2-methyl-5-norbornene 2-methyl carboxylic acid, 2-methyl-5-norbornene 2-carboxylic acid ethyl, 2-methyl-5-norbornene 2-carboxylic acid propyl, 2-methyl-5-norbornene 2-carboxylic acid butyl, 2-methyl-5-norbornene 2-carboxylic acid trifluoroethyl, 2-methyl-5-norbornene 2-yl ethyl acetate, 5-trimethoxysilyl 2-norbornene, 5-dimethoxy chlorosilyl 2-norbornene, 5-methoxy chloromethyl silyl 2-norbornene, 5-dimethoxy chlorosilyl 2-norbornene, 5-methoxy hydride methylsilyl 2-norbornene, 5-dimethoxy hydride silyl 2-norbornene, 5-methoxy dimethylsilyl 2-norbornene, 5-triethoxy silyl 2-norbornene, 5-diethoxy chlorosilyl 2-norbornene, 5-ethoxy chloromethyl silyl 2-norbornene, 5-diethoxy hydride silyl 2-norbornene, 5-ethoxy dimethylsilyl 2-norbornene, 5-ethoxydiethylsilyl 2-norbornene, 5-propoxy dimethylsilyl 2-norbornene, 5-triphenoxy silyl 2-norbornene, 5-diphenoxymethylsilyl 2-norbornene, 5-trimethoxysilyl methyl-2-norbornene, 5-(2-trimethoxysilyl) ethyl-2-norbornene, 5-(2-dimethoxy, chlorosilyl) ethyl-2-norbornene, 5-(1-trimethoxysilyl) ethyl-2-norbornene, 5-(2-trimethoxysilyl) propyl-2-norbornene, 5-(1-trimethoxysilyl) propyl-2-norbornene, 5-triethoxy silyl ethyl-2-norbornene, 5-dimethoxymethylsilylmethyl-2-norbornene, 5-trimethoxy propylsilyl 2-norbornene, 5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 5-norbornene 2-carboxylic acid triethoxy silyl propyl, 5-norbornene 2-carboxylic acid dimethoxy, methylsilylpropyl, 2-methyl-5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 2-methyl-5-norbornene 2-carboxylic acid dimethoxy, methylpropyl, 2-methyl-5-norbornene 2-carboxylic acid triethoxy silyl propyl, 5-norbornene 2,3-dimethyl dicarboxylate, 5-norbornene 2,3-diethyl dicarboxylate, the 5-norbornene 2, 3-carboxylic anhydride, N-phenyl-5-norbornene 2,3-carvoneimide, N-cyclohexyl-5-norbornene 2,3-carvoneimide, 3-tricyclo [4.3.0.1^{2,5}] decene, 4.3.0.1^{2,3,7}-tricyclo [5] decadiene (dicyclopentadiene), 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecen, 4.4.0.1^{2,5} 1^{7,8}-methyl-3-tetracyclo [10] dodecen, 8-methyl-8-carboxymethyl, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecen, 8-methyl-8-carboxyethyl, 4.4.0.1^{2,5} 1^{7,3}-tetracyclo [10] dodecen, etc. can be mentioned.

[0022] A repeating unit (c) shown by a general formula (3) constituted with a repeating unit (b) shown by repeating unit (a) shown by a general formula (1) and a general formula (2) is formed by carrying out addition copolymerization of "the specific alpha olefin."

[0023] As an example of specific alpha olefin, ethylene, propylene, 1-butene, 1-hexene, 1-octene, styrene, p-methylstyrene, o-methylstyrene, Although trimethylsilyl ethylene, triethyl silyl ethylene, trichlorosilyl ethylene, dimethyl chlorosilyl ethylene, methyl dichlorosilyl ethylene, triethoxy silyl ethylene, tripropoxy silyl ethylene, etc. are mentioned, Ethylene, styrene, and p-methylstyrene are preferred in these.

[0024] A copolymerization method of a copolymerization method of specific cyclic olefin (1) of this invention and specific cyclic olefin (2) or cyclic olefin (1) and cyclic olefin (2), and specific alpha olefin is performed by a following method.

[0025] As a typical polymerization catalyst, [Pd(CH₃ CN)₄] and [BF₄]₂, [Pd(PhCN)₄] [SbF₆]₂ di-mu-chloro-bis(6-methoxy bicyclo[2.2.1]hept 2-ene-, and sigma [5], 2pi)Pd (it abbreviates to "I" hereafter.), and methylalumoxane (it abbreviates to "MAO" hereafter.)

I, AgSbF₆ and I, AgBF₄, [(eta³-aryl) PdCl]₂ and AgSbF₆, [(eta³-aryl) PdCl]₂ and AgBF₄, [(eta³-clo chill) Pd (cyclo-octadiene)], [PF₆], [(1, 5-cyclo-octadiene) Pd. (CH₃) (Cl)], PPh₃, NaB[3 and 5-(CF₃)₂C₆H₃]₄ [(eta³-clo chill) nickel (cyclo-octadiene)], [B(CF₃) (2C₆H₄)₄]

[NiBr (NPM₃)₄], MAO, nickel(octanoate)₂ and MAO, nickel(octanoate)₂, B(C₆F₅)₃, and AlEt₃, nickel(octanoate)₂, a reactant of HSbF₆, BF₃ and Et₂O, and AlEt₃, nickel. (Octanoate)₂. A reactant of HSbF₆. A reactant and AlEtF₂nickel of BF₃ and Et₂O, reactant nickel(octanoate)₂ of AlEt₃, a reactant of HSbF₆, AlEt₂FNi(octanoate)₂, and HSbF₆. (Naphthoate) Reactant nickel of ₂, a reactant of HSbF₆, BF₃ and Et₂O, AlBu₃nickel(naphthoate)₂, a reactant of HSbF₆, B(C₆F₅)₃, and AlEt₃. (Octanoate)₂, Ph₃C-B(C₆F₅)₃, and AlEt₃, Bis[N-(3-tert-butylsalicylidene)phenylamino]nickel(II), Ph₃CB(C₆F₅)₄, and AlBu₃Bis[N-(3-tert-butylsalicylidene)phenylamino]nickel(II) and MAO, nickel[PhC. (O) CHPh₂]. (Ph). (PPh₃) nickel[OC. (O) (C₆H₄) PPh₂](H) (PPh₃) nickel(COD)₂ and PPh₃=CHC(O) Ph[(ArN=CHC₆H₃(O) (Anth)) (Ph)(PPh₃) nickel (here)) Ar: 2, 6-(Pr)₂C₆H₃, Pr:isopropyl, Anth:9-anthracene Toluene-nickel(C₆F₅)₂, [PPh₂CH₂C(O) Ph] nickel(C₆F₅)₂, A compound etc. which form a complex or cation complexes, such as nickel of periodic table 8 fellows, such as Co (neodecanoate) and MAO, Pd, and Co, are mentioned.

[0026]As a solvent, alicyclic hydrocarbon solvents, such as cyclohexane, cyclopentane, and methylcyclopentane, Aliphatic hydrocarbon solvents, such as pentane, hexane, heptane, and octane, Aromatic hydrocarbon solvents, such as toluene, benzene, and xylene, dichloromethane, Halogenated hydrocarbon solvents, such as 1,2-dichloroethylene and chlorobenzene, Ethyl acetate, butyl acetate, gamma-butyrolactone, propylene glycol, A solvent chosen from polar solvents, such as wood ether, nitromethane, N-methyl pyrrolidone, pyridine, N, N'-dimethylimidazolidinone, dimethylformamide, and an acetamide, etc. is used.

[0027]As the method of a polymerization, a monomer and a molecular weight modifier which become a reaction vessel from a solvent and cyclic olefin under nitrogen or argon atmosphere are taught, and a polymerization system is set as temperature of the range of -20 °C - 100 °C. Next, the above-mentioned catalyst component is added and it polymerizes in -20 °C - 100 °C. A weight ratio of a solvent/monomer is performed in 1-20. Regulation of a molecular weight is adjusted by the target molecular weight with an inversion rate and polymerization temperature to quantity of a polymerization catalyst, an addition of molecular weight modifiers, such as alpha olefin, hydrogen, and a diphenyl dihydrosilane, and a polymer. A stop of a polymerization is performed by compound chosen from water, alcohol, organic acid, carbon dioxide, etc. The water/alcoholic mixture of acid chosen as a polymer solution from organic carboxylic acid, such as lactic acid and oxalic acid, are added, and a catalyst residue is separated and removed from a polymer solution. A polymer is obtained by putting a polymer solution in alcohol chosen from methanol, ethanol, isopropanol, etc., solidifying it, and carrying out reduced pressure drying. At this process, an unreacted monomer which remains in a polymer solution is also removed.

[0028]A molecular weight of a cyclic olefin system copolymer of this invention, o-dichlorobenzene. a number average molecular weight of polystyrene conversion measured by a gel permeation chromatography used as a solvent -- 2,000-1,000,000, and weight average molecular weight -- 3,000-1,500,000 -- desirable -- a number average molecular weight -- 10,000-700,000. Weight average molecular weight is 20,000-1,000,000. Disruptive strength when a number average molecular weight uses less than 2,000 and weight average molecular weight considers it as a film, a thin film, and a sheet by less than 3,000 becomes insufficient in many cases. On the other hand, if a number average molecular weight exceeds 1,000,000 and weight average molecular weight exceeds 1,500,000, the molding workability of a sheet and a film will fall, or solution viscosity will become high at the time of film production of a cast film, and handling will become difficult.

[0029]glass transition temperature of a cyclic olefin system copolymer of this invention is called

for with peak temperature of temperature distribution of T_{δ} (a storage modulus $-- E' --$ a loss modulus $-- E'' --$ $Tan \delta = E'' / E'$) measured by dynamic viscoelasticity. 120-400 °C of glass transition temperature [200-370 °C of] of a cyclic olefin system copolymer of this invention is 250-350 °C especially preferably still more preferably. When glass transition temperature carries out liquid crystal group board formation in less than 120 °C at a film or a sheet shaped, heat resistance is insufficient, heat modification takes place, and it is not desirable. Since disassembly of a copolymer takes place on the other hand when performing processing in an elevated temperature, and crosslinking reaction, if glass transition temperature exceeds 400 °C, it is not desirable. A repeating unit (a) in a copolymer of this invention, For example, by an infrared absorption spectrum, can check by absorption of carbonyl (C=O) of a contiguity double bond of 1725-1735- cm^{-1} , etc., and with a nuclear magnetic resonance spectrum (1H -NMR). The structure can be checked from a peak of a proton of a carbon atom substituent of a 5.4-6.9 ppm C=C double bond. A rate of a repeating unit (a) in a copolymer can be searched for by 1H -NMR from a ratio of absorption of a 0.9-3.0 ppm proton, and absorption of a proton of a carbon atom substituent of a 5.4-6.9 ppm C=C double bond originating in all the norbornene structures.

[0030]In a cyclic olefin system copolymer of this invention, 2,6-di-tert-butyl-4-methylphenol, 4,4'-thiobis- (6-t-butyl-3-methyl phenol), 1,1'-bis(4-hydroxyphenyl)cyclohexane, 2,2'-methylenebis (4-ethyl-6-t-butylphenol), Phenol systems, such as 2,5-di-t-butylhydroquinone and pentaerythrityl tetrakis [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, To a hydroquinone system antioxidant pan, tris (4-methoxy-3,5-diphenyl) phosphite, Tris (nonylphenyl) phosphite, The Lynn system antioxidants, such as tris (2,4-di-t-butylphenyl) phosphite bis(2,6-di-t-butyl-4-methylphenyl)PENTAERI stole diphosphite bis(2,4-di-tert-butylphenyl) pentaerythritoldiphosphite, are added, Oxidation stability can be raised.

[0031]An oxide of at least one sort of metal chosen as a cyclic olefin system copolymer of this invention from a group of silicon, aluminum, titanium, and a zirconium, And a silicon oxide (these are also hereafter called "metallic oxide") produced by carrying out hydrolysis condensation of/or the alkoxy silane compound is blended, and it is good also as a complex.

[0032]As the above-mentioned complex, to a cyclic olefin system copolymer of above-mentioned this invention, the shape of colloidal one, It can also be considered as a complex which mixed the surface with what denaturalized by acrylic ester which has alkoxy silyl groups for metallic oxides, such as silica, alumina, and a titania, or methacrylic acid ester, and a metallic oxide distributed micro in a copolymer and for which a bridge can be constructed.

[0033]A complex which a metallic oxide distributed micro in a copolymer and for which a bridge can be constructed is obtained without carrying out surface denaturation of the above-mentioned metallic oxide, when a cyclic olefin system copolymer of this invention contains alkoxy silyl groups.

[0034]furthermore -- as the above-mentioned complex -- the inside of a copolymer of this invention -- alcoholic salts, such as Si, aluminum, Ti, and Zr, and an aryl salt -- for example, A tetramethoxy silane, a tetraethoxysilane, methyl trimetoxysilane, methyl triethoxysilane, trimethoxy aluminum, and TORIE -- an ibis -- sial minium. By solution states, after mixing, catalysts, such as compounds, such as Sn, Ti, Zr, Y, and aluminum, and °C HCl and HF, are used, and a hybrid complex which can construct a bridge with hydrolysis and a "sol-gel method" which carries out a polycondensation is obtained in tetraethoxytitanium, tetraethoxy zircon, etc. When 100 nm or less of these inorganic particles are preferably distributed by particle diameter of 10 nm or less in a copolymer, it becomes the complex heat resistance and whose dimensional

stability improved by optical transparency.

[0035]In a complex of this invention, loadings of the above-mentioned metallic oxide are usually five to 30 weight section preferably three to 50 weight section to cyclic olefin system copolymer 100 weight section of this invention.

[0036]A cyclic olefin system copolymer (or complex) of this invention, With an extruder, directly, can also consider it as a film and a sheet thin film, and, dissolve a copolymer (complex) in a solvent chosen from polar solvents, such as a hydrocarbon solvent, a halogenated hydrocarbon solvent, ketone, ether, ester, amine, amide, and urea, and pass casting and an evaporation process -- optics -- it can be made a transparent film and a sheet. A copolymer (complex) can also be fabricated and processed at a film and a sheet, evaporating a solvent with an extruder, after swelling a copolymer (complex) to these solvents.

[0037]A cyclic olefin system copolymer of this invention, Or in order for the complex to be able to construct a bridge with activity energy lines, such as light or an electron beam, and to promote bridge construction, Sensitizers, such as aromatic compounds, an aromatic carbonyl compound, and aromatic thiocarbonyl compounds, an organic and inorganic peroxide, a sulfide compound, a diazo compound, thiol compounds, etc. can be added in small quantities. As a light source used for bridge construction, light whose wavelength is 250 nm - 450 nm is used. Temperature is 0-150 ** and time of a cross-linking condition is 1 to 300 minutes.

[0038]A cyclic olefin system copolymer of this invention, its complex, and these bridging bodies, since it has outstanding optical transparency, heat resistance, and adhesion and adhesion - optics (optical material), such as a light guide plate, a polarization film, a liquid crystal panel, a phase difference film, a transparent conductive film, an OHP film, an optical disc, an optical fiber, and a lens, and electronic parts -- it is further used for a medical care container, a container, etc.

[0039]A cyclic olefin system copolymer (complex) of this invention, Since it has outstanding optical transparency, heat resistance, an adhesive property, and adhesion, a hydride and an addition (**) polymer of a conventionally publicly known norbornene system ring breakage (**) polymer. for example, JP,61-29260,A and JP,60-16870,A. JP,60-26024,A, JP,2-51511,A, JP,1-132625,A, JP,1-132626,A, JP,4-202404,A, JP,4-63807,A, JP,8-198919,A, the Patent Publication Heisei No. 508649 [nine to] gazette, the Patent Publication Heisei No. 505880 [11 to] gazette, JP,61-292601,A etc. can be blended and a thermoplastic polymer composition, nothing, outstanding heat resistance, an optical property (transparency, low birefringence), and adhesion and adhesion can be given.

[0040]In such a thermoplastic polymer composition, although a blending ratio of a cyclic olefin system copolymer of this invention and other polymers (**) is suitably chosen according to a kind of a cyclic olefin system copolymer of this invention, and other polymers (**), both compatibility, and the purpose of using a constituent, In order to obtain a polymer composition which has the outstanding heat resistance, a rate of a cyclic olefin system copolymer of this invention is 20 to 80 % of the weight still more preferably ten to 90% of the weight preferably five to 95% of the weight.

[0041]Such a thermoplastic polymer composition is obtained mechanical mixing which uses an extruder, a Banbury mixer, a kneader, a roll mill, etc., and by melting in a solvent and carrying out a solution blend. A film, a sheet, and a thin film can be obtained from such a thermoplastic polymer composition as well as a case of a cyclic olefin system copolymer of this invention.

[Translation done.]

EXAMPLE

[Example] Hereafter, although an example explains this invention still more concretely, this invention does not receive restriction at all according to these examples. A molecular weight, glass transition temperature, a refractive index, glass transition temperature, a coefficient of linear expansion, water absorption, and adhesion and adhesion were measured by the following method.

[0043] (1) Weight average molecular weight, a number average molecular weight : it measured at 120 °C by using o-dichlorobenzene as a solvent using H type column by TOSOH CORP. with the product 150C type gel-permeation-chromatography (GPC) device made by UOTAZU (WATERS). The obtained molecular weight is a standard polystyrene reduced property.

(2) Total light transmittance : based on ASTM-D1003, the 100-micrometer-thick film was used and total light transmittance was measured.

(3) Peak temperature of T_{δ} (glass transition temperature) : T_{δ} (ratio $E''/E' = T_{\delta}$ of storage-modulus E' and loss-modulus E'') of dynamic viscoelasticity was measured, and peak temperature of the temperature distribution was made into the glass transition temperature of a copolymer. The test frequency performed measurement of dynamic viscoelasticity using LEO Vibron DDV-01FP (product made from a cage ene tech) on the conditions whose single waveform and excitation amplitude is 10 Hz and a part for /and whose 4 °C excitation modes a heating rate is 2.5 micrometers.

Coefficient of linear expansion : (4) TMA (Thermal Mechanical Analysis) / SS6100 (made by the SEIKO instrument company) are used, After having fixed in the distance between zippers of 10 mm, once carrying out temperature up of the sample 100 micrometers of thickness, 3 mm in width, and 10 cm in length from a room temperature to about 200 °C and taking a residual strain, temperature up was carried out by 3 °C / min. from the room temperature, and the coefficient of linear expansion was calculated from the elongation of the distance between zippers.

(5) Water absorption : after making it immersed in underwater [23 °C] for 24 hours, water absorption was searched for from the weight change before and behind immersion.

An adhesive property and adhesion : (6) Vapor-deposit aluminum to a specimen (10 cm x 10 cm), and to this vacuum evaporation film by a cutter. The squares (1 mm x 1 mm) put in slitting, did the friction test by a cellophane tape, and measured ten pieces x the ten number of the blocks in 25 blocks which exfoliated so that it might be formed.

[0044] The synthetic example 1 [Composition of acrylic acid 2-(5-NORUBORUNENIRU) methyl]

50 g (0.403 mol) of 5-hydroxymethyl-2-norbornene and 39.2 ml (0.483 mol) of acrylic acid chloride are added to 370 ml of methylene chlorides in a 500-ml resisting pressure crow container and under a nitrogen atmosphere, Furthermore, it is triethylamine. 84.3 ml (0.605 mol) was added and it was made to react at 25 °C for 3 hours. Then, it flowed into the hydrochloric acid aqueous solution, the aqueous phase was neutralized by sodium carbonate, and the organic phase was separated by the separating funnel. 75 mg of pentaerythrityl tetrakis [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] which is polymerization inhibitor was added, and it distilled under 55 °C and 5mmHg. 47 g was obtained for acrylic acid 2-(5-NORUBONENIRU) methyl. (65% of yield)

[0045]Example 1 [Composition of the copolymer of 2-norbornene and acrylic acid 2-(5-NORUBORUNENIRU) methyl]

Toluene with a moisture of 5 ppm under a nitrogen atmosphere to a 300-ml pressure bottle 100 ml, 2-norbornene 90mmol. and acrylic acid 2-(5-NORUBORUNENIRU) methyl 10mmol. are taught, Antimony hexafluoride acid (HSbF_6) and octanoic acid nickel (nickel(oct)₂) at -30 °C beforehand, The denaturation octanoic acid nickel (HSbF_6 /nickel(oct)₂=1.2 mole ratio) made to react 0.04 mg-equivalent nickel, It added in order of trifluoride boron and ethyl ether complex 0.36mmol. triethylaluminum 0.40mmol., and the polymerization was performed at 30 °C for 2 hours. After adding to the above-mentioned copolymer solution and making 4 ml of isopropanols [60 °C of] containing lactic acid 4mmol. react to it for 30 minutes, it put into 600 ml of water, and it stirred, and settlement separation was carried out and the decatalyst was performed from the copolymer solution. Then, the copolymer solution was put into 1,000 ml of isopropanol, and was solidified, the unreacted monomer was removed, 80 °C of copolymers were dried for 10 hours, and the white powder 4.7g was obtained. The inversion rate to the copolymer of a monomer was 46%.

[0046]Analysis of a copolymer : - The $\text{CH}_2=$ proton 5.4 of the $\text{CH}_2=\text{CH}-\text{CO}-\text{O}$ -substituent originating in the 0.9-3.0 ppm proton peak and acrylic acid 2-(5-NORUBORUNENIRU) methyl originating in the norbornene structure measured by the presentation of 270 MHz of a copolymer, and ¹H-NMR. - the percentage of the structural unit which originates in acrylic acid 2-(5-NORUBORUNENIRU) methyl from 6.5 ppm was 3.2-mol %. The 5.0-5.3 ppm proton of the $-\text{CH}=\text{CH}-$ structure generated by the ring opening polymerization of norbornene structure was not observed. The ¹H-NMR chart of the obtained copolymer is shown in drawing 1.

- Qualitative analysis of a functional group : the characteristic absorption of the ester group of $1,727\text{-cm}^{-1}$ by $\text{CH}_2=\text{CH}-\text{CO}-\text{O}$ - and the characteristic absorption of $1,636\text{-cm}^{-1}$ by $\text{C}=\text{C}$ were observed with the infrared absorption spectrum. The infrared absorption spectrum of the obtained copolymer is shown in drawing 2.

- Molecular weight : the number average molecular weight of the standard polystyrene conversion measured by GPC was 108,000, and weight average molecular weight was 233,000.

- Glass transition temperature : the peak temperature (glass transition temperature) of temperature distribution of T_{delta} was 350 °C.

- Total light transmittance : the total light transmittance measured using a 100-micrometer-thick film was 91%.

[0047]The with a crosslinking treatment [100-micrometer thickness unconstructed a bridge] cast film dissolved in toluene at 25 °C. When the high-pressure mercury lamp of 500W was used for this film and the main peak of wavelength irradiated with 314, 366, and the ultraviolet rays that are 405 or 436 nm at 30 °C via the heat ray cut-off filter for 30 minutes, the film became insoluble to 25 °C toluene.

[0048]Instead of example 2 acrylic-acid 2-(5-NORUBONENIRU) methyl, it polymerized like Example 1 except using methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl) methyl. The inversion rate to the copolymer of a monomer was 82%. The percentage of the structural unit originating in methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}.] dodecenyl) methyl in a copolymer was 9.5-mol% from ¹H-NMR analysis. The number average molecular weight by GPC was 113,000, and weight average molecular weight was 226,000. By the exposure of ultraviolet rays, it became 25 °C toluene with the completely insoluble film like Example 1. When 90 °C of films which obtained benzoyl peroxide by carrying out 0.5 weight-section addition per polymer 100 weight section were heat-treated for 15 minutes, it became 25 °C and

toluene with the completely insoluble film.

[0049] Instead of example 3 methacrylic-acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl 10mmol, Except using methacrylic acid 3-(8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl) methyl 5mmol and 5-triethoxy silyl 2-norbornene 5mmol, it polymerized like Example 1 and the copolymer 7.3g was obtained. Methacrylic acid 3 - (the percentage of the structural unit originating in 8-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] dodecenyl methyl was 4.8-mol % from ¹H-NMR analysis.) The rate of the structural unit originating in 5-triethoxy silyl 2-norbornene, It asked by infrared analysis from the analytical curve of the relative ratio of absorption of end CH₃ of the -Si-O-CH₂CH₃ group of 1,389-cm⁻¹, and absorption of -CH- by the norbornene skeleton of 1,294-cm⁻¹, and was 4.5-mol %. The number average molecular weight of this copolymer was 109,000, and weight average molecular weight was 214,000. A 100-micrometer film was created like Example 1, and bridge construction by ultraviolet rays was performed. It was completely insoluble to 25 ** toluene in the film. The total light transmittance of this film was 91%. There was no block with which the peel test of aluminum also exfoliates.

[0050] It is a silica particle (the mean particle diameter of 12 nm) in 400 ml of example 4 methyl ethyl ketone. Specific surface area ² of 400 m, surface silanol 5micromol/m², Or 50 g of meta-cloxy (propyl) trimethoxysilane is added for an alumina particle (mean particle diameter of 20 nm, specific surface area ² of 150 m) to 100 g, respectively, Furthermore, a 1.5-g maleic anhydride was added to 10 ml of water as a catalyst, and it returned under nitrogen for 2 hours. 200 ml was removed from this solution under decompression of methyl ethyl ketone, and 200 ml of toluene was added. Thus, five weight sections were mixed for obtained colloidal silica or alumina of surface denaturation in the toluene solution to copolymer 100 weight of Example 3, and the composite-ized transparent solution was obtained. Next, the cast of the solution was carried out and about 100-micrometer film was obtained. The weighted solidity of the composite-ized film and the film which carried out optical bridge construction is shown in Table 1.

[0051]

[Table 1]

[0052] In example 5 Example 1, it carried out like Example 1 instead of acrylic acid 2-(5-NORUBORUNENIRU) methyl except using 2-hydroxyethyl methacrylic acid ester and ester of 2-methyl and 5-norbornene 2-carboxylic acid. The inversion rate to the polymer was 38%. The polymer was dissolved with toluene and the characteristic absorption of 1,727-cm⁻¹ by CH₂=CH-CO-O- was observed in the infrared absorption spectrum after acetone solidifies and refines. The percentage of the structural unit originating in this structure was 2.8-mol % among all the repeating units. The number average molecular weight of the polymer was 39,000, and weight average molecular weight was 66,000. Like Example 1, the bridge construction by light took

place and it was insoluble to toluene.

[0053] In comparative example 1 Example 1, instead of 2-norbornene 90mmol and acrylic acid 2-(5-NORUBORUNENIRU) methyl 10mmol, Using 2-norbornene 93mmol and 5-ethylidene-2-norbornene 7mmol, except using cyclohexane as a solvent, the copolymerization reaction was performed like Example 1 and the copolymer 7.6g was obtained. The number average molecular weight by GPC was 98,000, and weight average molecular weight was 198,000. Although a 100-micrometer film was created like Example 1 and the film was irradiated with ultraviolet rays, it mostly dissolved in cyclohexane. The remaining thing did not retain the original form with pastiness, either. Although benzoyl peroxide was added like Example 2 and the film was created and heated, it dissolved in cyclohexane. When the peel test of aluminum was carried out, it exfoliated altogether and adhesion was remarkably weak.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a chart of ^1H -NMR of the copolymer obtained in Example 1.

[Drawing 2] It is an infrared absorption spectrum of the copolymer obtained in Example 1.

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(54) 【発明の名称】 環状オレフィン系共重合体、この複合体、これらの架橋体、および光学材料

(57) 【要約】

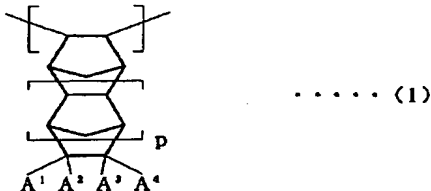
【課題】 優れた耐熱性、透明性、耐薬品性、耐溶剤性および接着・密着性を付与する、架橋可能な環状オレフィン系共重合体、この複合体、これらの架橋体、これらを用いた光学材料を提供すること。

【解決手段】 特定の架橋可能な官能基を有する環状オレフィンとそれ以外の環状オレフィンとを付加共重合した、重量平均分子量が3,000~1,500,000である、環状オレフィン系共重合体、これに特定の金属酸化物を配合した複合体、これらの架橋体、およびこれらを用いた光学材料。

【特許請求の範囲】

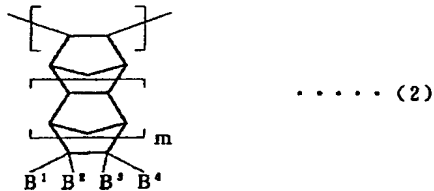
【請求項1】 下記一般式(1)で表される繰り返し単位(a)と下記一般式(2)で表される繰り返し単位(b)を含み、ポリスチレン換算重量平均分子量が3,000~1,500,000である環状オレフィン系共重合体。

【化1】



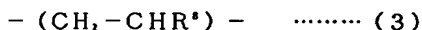
【式(1)中、A¹、A²、A³、A⁴はそれぞれ独立して、水素原子、炭素数1~20の炭化水素基、または、一般式-(CH₂)ᶠ-O-C(O)CR¹=CR²R³または一般式-C(O)-O-(CH₂)ᵍ-O-C(O)-CR¹=CR²R³で表される架橋可能な官能基を示し、A¹、A²、A³、A⁴のうち少なくとも一つは上記架橋可能な官能基である。ここで、R¹、R²、R³はそれぞれ独立に、水素原子、1~10のアルキル基を示す。fは0~3の整数、gは1~3の整数を示す。pは0~3の整数を示す。】

【化2】



【式(2)中、B¹、B²、B³、B⁴はそれぞれ独立して、水素原子、炭素数1~20のアルキル基、シクロアルキル基、アリール基、アルケニル基、ハロゲン原子、ハロゲン化炭化水素基、または-(CH₂)ₓ-Xで表される極性基を示す。ここで、Xは-C(O)OR⁴、-O-C(O)R⁵、または-Si(OR⁶)₃-R⁷であり、R⁴、R⁵は炭素数1~20のアルキル基、アリール基、シクロアルキル基またはこれらのハロゲン置換基、R⁶は炭素数1~10のアルキル基、アルケニル基またはアリール基で、R⁷はハロゲン原子、炭素数1~10のアルキル基、アルケニル基またはアリール基である。また、B¹とB²は、互いに結合して形成されるビニリデン、イミド、カルボン酸無水物基であってもよい。qは0~3の整数を示す。kは0~3の整数である。mは0または1の整数を示す。】

【請求項2】 さらに、下記一般式(3)で表される繰り返し単位(c)を含む請求項1記載の環状オレフィン系共重合体。



【式(3)中、R⁸は水素原子、炭素数1~8のアルキ

ル基、炭素数6~15のアリール基あるいは一般式-Si(R⁹)(R¹⁰)₃で表されるシリル基である。ここでR⁹は炭素数1~5のアルキル基またはアルコキシ基を示し、R¹⁰はハロゲン原子または水素原子を示す。tは0~3の整数である。】

【請求項3】 一般式(1)で示される繰り返し単位(a)が、全繰り返し単位中に0.1~30モル%含まれる請求項1または2記載の環状オレフィン系共重合体。

10 【請求項4】 一般式(2)のB¹、B²、B³、B⁴のうち少なくとも一つがアルコキシシリル基である繰り返し単位(b)が、全繰り返し単位中に0.1~20モル%含まれる請求項1または2記載の環状オレフィン系共重合体。

【請求項5】 請求項1~4いずれか1項記載の環状オレフィン系共重合体に、ケイ素、アルミニウム、チタンおよびジルコニウムの群から選ばれた少なくとも1種の金属の酸化物、ならびに/またはアルコキシシラン化合物を加水分解・縮合して得られるシリコン酸化物を配合してなる複合体。

20 【請求項6】 請求項1~4いずれか1項記載の環状オレフィン系共重合体、または、請求項5記載の複合体、を架橋させた架橋体。

【請求項7】 請求項1~4いずれか1項記載の環状オレフィン系共重合体、請求項5記載の複合体、または、請求項6記載の架橋体、を用いた光学材料。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、架橋可能な環状オレフィン系共重合体に関する。さらに詳しくは、優れた耐熱性、耐溶剤性、耐薬品性を有する光学材料に好適な架橋可能な環状オレフィン系共重合体、この複合体、これらの架橋体、およびこれらを用いた光学材料に関する。

【0002】

【従来の技術】近年、軽量化、小型・高密度化の要求に伴い、電子部品、光学部品など分野では、ガラスから、軽く、加工が容易な透明樹脂への転換が進んでいる。ガラスの代替としての透明樹脂は、加工しやすい、割れにくい、軽いなどの長所もあるが、耐熱性、耐久性・耐薬品性、寸法安定性が劣るなど欠点もある。そのため、これら欠点を改良することが求められている。

【0003】これまでに、光学的に透明性が高くかつ耐熱性のある重合体として、環状オレフィンの付加重合体が有用とされ、例えば、下記の特許が提案されている。

特開平03-205408号公報

特開平04-63807号公報

特開平07-104474号公報

特開平09-508649号公報

50 特開平10-251343号公報

特開平10-182799号公報

WO-98/20394号公報

WO-97/20871号公報

WO-96/37526号公報

WO-98/56839号公報

【0004】また、耐熱性、耐薬品性、寸法安定性の改良手段として架橋化が有力な手段であるとされており、以下の特許公報において、架橋可能な環状オレフィン系重合体として

(1) 特開平03-205408号公報にて、ビニル基、ビニリデン基で代表される炭化水素の不飽和結合を側鎖に有する環状オレフィン系付加重合体。

(2) WO-96/37526号公報にて、芳香族基を含む共役二重結合からなる置換基を側鎖に有する環状オレフィン系付加重合体。

(3) WO98/56839号公報、WO97/20871号公報、WO98/20394号公報にて、代表として、アルコキシシリル基を側鎖に含む環状オレフィン系付加重合体。特開平07-104474号公報にてグラフト反応によりアルコキシシリル基が導入された環状オレフィン系重合体。

(4) 特開平10-182799号公報および特開平10-251343号公報にて、エポキシ変性された環状オレフィン系重合体。などが開示されている。

【0005】しかし、架橋可能な反応部位としてのビニル基、ビニリデン基などの炭化水素からなる不飽和結合基では、架橋するために、熱、光などで分解して、ラジカルが発生する開始剤化合物が多く必要である。また、アルコキシシリル基の場合では、水、酸、有機スズ、アルミニウムジケトンなどの添加剤、触媒または光で分解する酸発生剤などが必要である。光学材料、電子材料用などの用途分野では、揮発性の不純物、触媒金属残さなど出来るだけ重合体中に含まれないことが求められている。そのため、架橋可能な反応部位としての官能基が有効に働き、架橋に際しても、出来るだけ少ない量の添加剤、触媒などを用いるかまたはこれらを用いない方法で架橋されることが求められている。

【0006】

【発明が解決しようとする課題】本発明は、上述の問題に鑑みなされたもので、優れた耐熱性、透明性、耐薬品性、耐溶剤性および接着・密着性を付与する、架橋可能な環状オレフィン系共重合体、その複合体、およびその架橋体を提供することを目的とする。さらに、架橋された環状オレフィン系共重合体ができるだけ架橋に際しての不純物、残さを含まない架橋体を提供することを目的とする。

【0007】

【課題を解決するための手段】本発明は、下記一般式

(1) で表される繰り返し単位 (a) と下記一般式

(2) で表される繰り返し単位 (b) を含み、ポリスチ 50

(3)

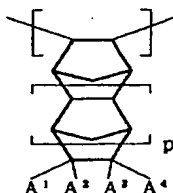
特開2002-293843

4

レン換算重量平均分子量が3,000~1,500,000である環状オレフィン系共重合体に関する。

【0008】

【化3】

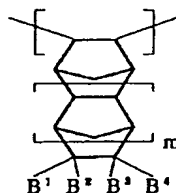


..... (1)

【0009】【式(1)中、A¹、A²、A³、A⁴はそれぞれ独立して、水素原子、炭素数1~20の炭化水素基、または、一般式-(CH₂)ᶠ-O-C(O)CR¹=CR²R³または一般式-C(O)-O-(CH₂)ᵍ-O-C(O)-CR¹=CR²R³で表される架橋可能な官能基を示し、A¹、A²、A³、A⁴のうち少なくとも一つは上記架橋可能な官能基である。ここで、R¹、R²、R³はそれぞれ独立に、水素原子、1~10のアルキル基を示す。fは0~3の整数、gは1~3の整数を示す。pは0~3の整数を示す。】

【0010】

【化4】



..... (2)

【0011】【式(2)中、B¹、B²、B³、B⁴はそれぞれ独立して、水素原子、炭素数1~20のアルキル基、シクロアルキル基、アリール基、アルケニル基、ハロゲン原子、ハロゲン化炭化水素基、または-(CH₂)ₓ-Xで表される極性基を示す。ここで、Xは-C(O)OR⁵、-OC(O)R⁵、または-Si(O)R⁶)₃、R⁵、R⁶は炭素数1~20のアルキル基、アリール基、シクロアルキル基またはこれらのハロゲン置換基、R⁵は炭素数1~10のアルキル基、アルケニル基またはアリール基で、R⁶はハロゲン原子、炭素数1~10のアルキル基、アルケニル基またはアリール基である。また、B¹とB²で形成されるビニリデンル、イミド、カルボン酸無水物基であってもよい。qは0~3の整数を示す。kは0~3の整数である。mは0または1の整数を示す。】ここで、上記環状オレフィン系共重合体は、さらに下記一般式(3)で表される繰り返し単位(c)を含むものでもよい。

- (CH₂-CHR⁷) - (3)

【式(3)中、R⁷は水素原子、炭素数1~8のアルキル基、炭素数6~15のアリール基あるいは一般式-Si(R⁸)₃、(R⁸)₃で表されるシリル基である。ここでR⁸は炭素数1~5のアルキル基またはアルコキシ

基を示し、 R^{10} はハロゲン原子または水素原子を示す。 t は0~3の整数である。]また、上記環状オレフィン系共重合体を構成する一般式(1)で示される繰り返し単位(a)は、全繰り返し単位中に0.1~30モル%含まれるものが好ましい。さらに、上記環状オレフィン系共重合体を構成する一般式(2)の B^1 、 B^2 、 B^3 、 B^4 のうち少なくとも一つがアルコキシシリル基である繰り返し単位(b)は、全繰り返し単位中に0.1~20モル%含まれるものが好ましい。本発明の環状オレフィン系共重合体には、ケイ素、アルミニウム、チタンおよびジルコニウムの群から選ばれた少なくとも1種の金属の酸化物、ならびに/またはアルコキシシラン化合物を加水分解・縮合して得られるシリコン酸化物を配合し、複合体としてもよい。次に、本発明は、上記環状オレフィン系共重合体、または上記複合体、を架橋させるなる架橋体に関する。次に、本発明は、上記環状オレフィン系共重合体、上記複合体、または、上記架橋体、を用いた光学材料に関する。

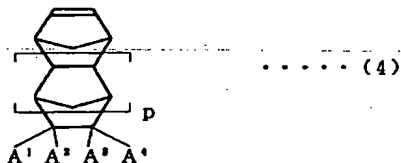
[0012]

【発明の実施の形態】以下に本発明の実施の形態を具体的に説明する。本発明の環状オレフィン系共重合体は、一般式(1)に示す繰り返し単位(a)および一般式(2)に示す繰り返し単位(b)を含む環状オレフィン系共重合体、または一般式(1)に示す繰り返し単位(a)、一般式(2)に示す繰り返し単位(b)および一般式(3)で示す繰り返し単位(c)を含む環状オレフィン系共重合体である。

【0013】一般式(1)で示される繰り返し単位(a)は、下記一般式(4)に示す環状オレフィン(以下、「特定の環状オレフィン(1)」という)の付加重合により、形成することができる。

[0014]

[化5]



【0015】[式(4)中、 A^1 、 A^2 、 A^3 、 A^4 および p は式(1)に示すものと同じである。]

本発明の環状オレフィン系共重合体に繰り返し単位(a)の割合が0.1~30モル%含まれていると、光、熱により、容易に架橋が可能となる。その割合が0.1%未満では架橋がかかりにくくなり、一方、30モル%を超えると、貯蔵安定性が劣るようになる。繰り返し単位(a)の割合は、好ましくは0.5~10モル%である。

【0016】本発明の繰り返し単位(a)には、一般式(1)に示した2, 3付加構造単位の他に、2, 7付加

構造単位が少量含まれていてもよい。

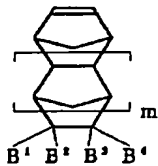
【0017】特定の環状オレフィン(1)の具体例としては、アクリル酸2-(5-ノルボルネニル)メチル(別称: 2-ヒドロキシメチル-5-ノルボルネンとアクリル酸のエステル)、アクリル酸2-(3-メチル-5-ノルボルネニル)メチル、アクリル酸2-(3-エチル-5-ノルボルネニル)メチル、メタクリル酸2-(5-ノルボルネニル)メチル、アクリル酸2-(5-ノルボルネニル)エチル、メタクリル酸2-(5-ノルボルネニル)エチル、アクリル酸5-ノルボルネニル、アクリル酸2-メチル-5-ノルボルネニル、メタクリル酸5-ノルボルネニル、メタクリル酸2-メチル-5-ノルボルネニル、アクリル酸3-(3-メチル-8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)メチル、アクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)メチル、メタクリル酸3-(3-メチル-8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)メチル、メタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)メチル、アクリル酸3-(3-メチル-8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)、アクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)、メタクリル酸3-(3-メチル-8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)、メタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)

クロトン酸2-(5-ノルボルネニル)メチル、クロトン酸3-(3-メチル-8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}]ドデセニル)、2-ヒドロキシエチルアクリレートと5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシエチルメタクリレートと5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシエチルアクリレートと2-メチル-5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシエチルメタクリレートと2-メチル-5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシプロピルアクリレートと5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシプロピルメタクリレートと5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシプロピルアクリレートと2-メチル-5-ノルボルネン-2-カルボン酸のエステル、2-ヒドロキシプロピルメタクリレートと2-メチル-5-ノルボルネン-2-カルボン酸のエステルなどが挙げられる。

【0018】一般式(2)で示される繰り返し単位(b)は、下記一般式(5)に示す環状オレフィン(以下、「特定の環状オレフィン(2)」という)の付加重合により、形成することができる。

[0019]

[化6]



..... (5)

【0020】〔式(5)中、 B^1 、 B^2 、 B^3 、 B^4 および m は式(2)と同様である。〕

本発明の環状オレフィン系共重合体を構成する一般式 (2)の B^1 、 B^2 、 B^3 、 B^4 のうち少なくとも一つがアルコキシシリル基である繰り返し単位(b)は、全繰り返し単位中に0.1~20モル%含まれるものが、金属酸化物またはアルコキシシラン化合物の縮合体をミクロに分散し、光学的に透明性の高い複合体とするためや、他の部材との接着性を高めるために好ましい。さらに、好ましくは0.5~10モル%である。

【0021】特定の環状オレフィン(2)の具体例としては、2-ノルボルネン、5-メチル-2-ノルボルネン、5-エチル-2-ノルボルネン、5-プロピル-2-ノルボルネン、5-ブチル-2-ノルボルネン、5-ペンチル-2-ノルボルネン、5-ヘキシル-2-ノルボルネン、5-ヘプチル-2-ノルボルネン、5-オクチル-2-ノルボルネン、5-デシル-2-ノルボルネン、5-ドデシル-2-ノルボルネン、5,6-ジメチル-2-ノルボルネン、5-メチル-5-エチル-2-ノルボルネン、5-フェニル-2-ノルボルネン、5-ビニル-2-ノルボルネン、5-アリル-2-ノルボルネン、5-イソプロピリデン-2-ノルボルネン、5-エチリデン-2-ノルボルネン、5-シクロヘキシル-2-ノルボルネン、5-シクロヘキセニル-2-ノルボルネン、5-インデニル-2-ノルボルネン、5,6-インダン-2-ノルボルネン、5-フロロ-2-ノルボルネン、5-クロロ-2-ノルボルネン、5-ノルボルネン-2-カルボン酸メチル、5-ノルボルネン-2-カルボン酸エチル、5-ノルボルネン-2-カルボン酸ブチル、2-メチル-5-ノルボルネン-2-カルボン酸メチル、2-メチル-5-ノルボルネン-2-カルボン酸エチル、2-メチル-5-ノルボルネン-2-カルボン酸プロピル、2-メチル-5-ノルボルネン-2-カルボン酸ブチル、2-メチル-5-ノルボルネン-2-カルボン酸トリフロロエチル、2-メチル-5-ノルボルネン-2-イル酢酸エチル、5-トリメトキシシリル-2-ノルボルネン、5-ジメトキシクロロシリル-2-ノルボルネン、5-メトキシクロロメチルシリル-2-ノルボルネン、5-ジメトキシクロロシリル-2-ノルボルネン、5-メトキシヒドリドメチルシリル-2-ノルボルネン、5-ジメトキシヒドリドシリル-2-ノルボルネン、5-メトキシジメチルシリル-2-ノルボルネン、5-トリエトキシシリル-2-ノルボルネン、5-ジエトキシクロロシリル-2-ノルボルネン、

5-エトキシクロロメチルシリル-2-ノルボルネン、5-ジエトキシヒドリドシリル-2-ノルボルネン、5-エトキシジメチルシリル-2-ノルボルネン、5-エトキシジエチルシリル-2-ノルボルネン、5-プロポキシジメチルシリル-2-ノルボルネン、5-トリフェノキシシリル-2-ノルボルネン、5-ジフェノキシメチルシリル-2-ノルボルネン、5-トリメトキシシリルメチル-2-ノルボルネン、5-(2-トリメトキシシリル)エチル-2-ノルボルネン、5-(2-ジメトキシ、クロロシリル)エチル-2-ノルボルネン、5-(1-トリメトキシシリル)エチル-2-ノルボルネン、5-(2-トリメトキシシリル)プロピル-2-ノルボルネン、5-(1-トリメトキシシリル)プロピル-2-ノルボルネン、5-トリエトキシシリルエチル-2-ノルボルネン、5-ジメトキシメチルシリルメチル-2-ノルボルネン、5-トリメトキシプロピルシリル-2-ノルボルネン、5-ノルボルネン-2-カルボン酸トリメトキシシリルプロピル、5-ノルボルネン-2-カルボン酸トリエトキシシリルプロピル、5-ノルボルネン-2-カルボン酸ジメトキシ、メチルシリルプロピル、2-メチル-5-ノルボルネン-2-カルボン酸トリメトキシシリルプロピル、2-メチル-5-ノルボルネン-2-カルボン酸ジメトキシ、メチルプロピル、2-メチル-5-ノルボルネン-2-カルボン酸トリエトキシシリルプロピル、5-ノルボルネン-2,3-ジカルボン酸ジメチル、5-ノルボルネン-2,3-ジカルボン酸ジエチル、5-ノルボルネン-2,3-カルボン酸無水物、N-フェニル-5-ノルボルネン-2,3-カルボンイミド、N-シクロヘキシル-5-ノルボルネン-2,3-カルボンイミド、3-トリシクロ[4.3.0.1^{2,3}]デセン、3,7-トリシクロ[4.3.0.1^{2,3}]デカジェン(ジシクロペンタジェン)、3-テトラシクロ[4.4.0.1^{2,3}.1^{7,10}]ドデセン、8-メチル-3-テトラシクロ[4.4.0.1^{2,3}.1^{7,10}]ドデセン、8-メチル-8-カルボキシメチル、3-テトラシクロ[4.4.0.1^{2,3}.1^{7,10}]ドデセン、8-メチル-8-カルボキシエチル、3-テトラシクロ[4.4.0.1^{2,3}.1^{7,10}]ドデセン、などを挙げることができる。

【0022】一般式(1)で示される繰り返し単位(a)および一般式(2)で示される繰り返し単位(b)とともに構成される一般式(3)で示される繰り返し単位(c)は、「特定の α -オレフィン」を付加共重合することにより形成される。

【0023】特定の α -オレフィンの具体例としては、エチレン、プロピレン、1-ブテン、1-ヘキセン、1-オクテン、スチレン、p-メチルスチレン、o-メチルスチレン、トリメチルシリルエチレン、トリエチルシリルエチレン、トリクロロシリルエチレン、ジメチルクロロシリルエチレン、メチルジクロロシリルエチレン、

トリエトキシシリルエチレン、トリプロポキシシリルエチレン、などが挙げられるが、これらの中でエチレン、スチレン、p-メチルスチレンが好ましい。

【0024】本発明の特定の環状オレフィン(1)と特定の環状オレフィン(2)の共重合方法、あるいは、環状オレフィン(1)と環状オレフィン(2)および特定の α -オレフィンの共重合方法は、下記の方法によって行われる。

【0025】代表的な重合触媒としては、

$[\text{Pd}(\text{CH}_3\text{CN})_4]$ 、 $[\text{BF}_4]^-$ 、 $[\text{Pd}(\text{PhCN})_4]$ 、 $[\text{SbF}_6]^-$ 、ジ- μ -クロロ-ビス(6-メトキシピシクロ[2.2.1]ヘプト-2-エン-エンド-5 σ , 2 π)Pd (以下、「I」と略す。)とメチルアルモキサン(以下、「MAO」と略す。)

Iと AgSbF_6 、Iと AgBF_4 、

$[(\eta^1\text{-アリール})\text{PdCl}]_2$ と AgSbF_6 、 $[(\eta^1\text{-アリール})\text{PdCl}]_2$ と AgBF_4 、

$[(\eta^1\text{-クロチル})\text{Pd}(\text{シクロオクタジエン})]$ $[\text{PF}_6]^-$ 、

$[(1,5\text{-シクロオクタジエン})\text{Pd}(\text{CH}_3)(\text{Cl})]$ と PPh_3 と $\text{NaB}[3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3]$ 、

$[(\eta^1\text{-クロチル})\text{Ni}(\text{シクロオクタジエン})]$ $[\text{B}(\text{CF}_3)_4]^-$

$[\text{NiBr}(\text{NPM}_2)_2]$ と MAO 、 $\text{Ni}(\text{オクトエート})_2$ と MAO 、

$\text{Ni}(\text{オクトエート})_2$ と $\text{B}(\text{C}_6\text{F}_5)_3$ と AlEt_3 、

$\text{Ni}(\text{オクトエート})_2$ と HSbF_6 の反応物と $\text{BF}_3 \cdot \text{Et}_2\text{O}$ と AlEt_3 、

$\text{Ni}(\text{オクトエート})_2$ と HSbF_6 の反応物と $\text{BF}_3 \cdot \text{Et}_2\text{O}$ と AlEt_3 の反応物

$\text{Ni}(\text{オクトエート})_2$ と HSbF_6 の反応物と AlEt_3 、

$\text{Ni}(\text{オクトエート})_2$ と HSbF_6 の反応物と AlEt_3 、

$\text{Ni}(\text{ナフトエート})_2$ と HSbF_6 の反応物と $\text{BF}_3 \cdot \text{Et}_2\text{O}$ と AlB u_3 、

$\text{Ni}(\text{ナフトエート})_2$ と HSbF_6 の反応物と $\text{B}(\text{C}_6\text{F}_5)_3$ と AlEt_3 の反応物

$\text{Ni}(\text{オクトエート})_2$ と $\text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ と AlEt_3 、

$\text{Bis}[N-(3\text{-tert-butylsalicylidene})\text{phenylamino}] \text{Ni(II)}$ と $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_3$ と Al i Bu_3 、

$\text{Bis}[N-(3\text{-tert-butylsalicylidene})\text{phenylamino}] \text{Ni(II)}$ と MAO 、

$\text{Ni}[\text{PhC}(\text{O})\text{CHPPh}_2](\text{Ph})_2(\text{PPh}_3)\text{Ni}[\text{OC}(\text{O})(\text{C}_6\text{H}_4)\text{PPh}_2](\text{H})(\text{PPh}_3)\text{Ni}(\text{COD})_2$ と $\text{PPh}_3 = \text{CHC}(\text{O})\text{Ph}$

$[(\text{ArN}=\text{CHC}_6\text{H}_4(\text{O})(\text{Anth}))](\text{Ph})(\text{PPh}_3)\text{Ni}$ (ここで、 Ar : 2, 6-(Pr) $_2\text{C}_6\text{H}_3$ 、Pr: isopropyl、Anth: 9-anthracene)

$\text{Toluene} \cdot \text{Ni}(\text{C}_6\text{F}_5)_2$ 、

$[\text{PPh}_3\text{CH}_2\text{C}(\text{O})\text{Ph}]\text{Ni}(\text{C}_6\text{F}_5)_2$ 、

$\text{Co}(\text{ネオデカノエート})$ と MAO

などの周期律表8族のNi、Pd、Coなどの錯体またはカチオン錯体を形成する化合物などが挙げられる。

【0026】溶媒としては、シクロヘキサン、シクロペンタン、メチルシクロペンタンなどの脂環式炭化水素溶媒、ペンタン、ヘキサン、ヘプタン、オクタンなどの脂肪族炭化水素溶媒、トルエン、ベンゼン、キシレンなどの芳香族炭化水素溶媒、ジクロロメタン、1, 2-ジクロロエチレン、クロロベンゼンなどのハロゲン化炭化水素溶媒、酢酸エチル、酢酸ブチル、 γ -ブチロラクトン、プロピレングリコール、ジメチルエーテル、ニトロメタン、N-メチルピロリドン、ピリジン、N, N'-ジメチルイミダゾリジノン、ジメチルフォルムアミド、アセトアミドなどの極性溶媒などから選ばれた溶媒が用いられる。

【0027】重合の方法としては、窒素またはアルゴン雰囲気下で反応容器に溶媒と環状オレフィンからなるモノマーと分子量調節剤を仕込み、 $-20^\circ\text{C} \sim 100^\circ\text{C}$ の範囲の温度に重合系を設定する。次に、上記触媒成分を添加して $-20^\circ\text{C} \sim 100^\circ\text{C}$ の範囲で重合を行う。溶媒/モノマーの重量比は、1~20の範囲で行われる。分子量の調節は、重合触媒の量と α -オレフィン、水素、ジフェニルジヒドロシランなどの分子量調節剤の添加量、重合体への転化率および重合温度によって、目的とする分子量に調節される。重合の停止は、水、アルコール、有機酸、炭酸ガスなどから選ばれた化合物により行われる。重合体溶液に乳酸、シュウ酸など有機カルボン酸から選ばれた酸の水/アルコール混合物を添加して、触媒残さは重合体溶液から分離・除去される。重合体は、重合体溶液をメタノール、エタノール、イソプロパノールなどから選ばれたアルコール中に入れて、凝固し、減圧乾燥することにより得られる。この工程で、重合体溶液に残存する未反応モノマーも除去される。

【0028】本発明の環状オレフィン系共重合体の分子量は、 α -ジクロロベンゼンを溶媒とするゲル・パーミエーションクロマトグラフィーで測定されるポリスチレン換算の数平均分子量が2, 000~1, 000, 000、重量平均分子量が3, 000~1, 500, 000、好ましくは数平均分子量が10, 000~700, 000、重量平均分子量が20, 000~1, 000, 000である。数平均分子量が2, 000未満、重量平均分子量が3, 000未満では、フィルム、薄膜およびシートとしたときの破壊強度が不十分となることが多い。一方、数平均分子量が1, 000, 000、重量平均分子量が1, 500, 000を超えると、シート、フィルムの成形加工性が低下したり、キャストフィルムの製膜時、溶液粘度が高くなり、取扱いが困難となる。

【0029】本発明の環状オレフィン系共重合体のガラス転移温度は、動的粘弾性で測定される $\text{Tan } \delta$ (貯蔵弾性率 E' 、損失弾性率 E'' 、 $\text{Tan } \delta = E''/E'$)の温度分散のピーク温度で求められる。本発明の環状オレフィン系共重合体のガラス転移温度は、好ましくは120~400 $^\circ\text{C}$ 、さらに好ましくは200~370 $^\circ\text{C}$ 、

特に好ましくは250～350℃である。ガラス転移温度が120℃未満では、フィルムまたはシート状に液晶基盤形成する際に耐熱性が不足して、熱変形が起こり好ましくない。一方、ガラス転移温度が400℃を超えると、高温での加工、架橋反応を行う際に共重合体の分解が起こるため好ましくない。なお、本発明の共重合体中の繰り返し単位(a)は、例えば、赤外線吸収スペクトルによって、1725～1735 cm⁻¹の隣接二重結合のカルボニル(C=O)の吸収などにより確認でき、また、核磁気共鳴スペクトル(¹H-NMR)により、5.4～6.9 ppmのC=C二重結合の炭素原子置換基のプロトンのピークから、その構造を確認することができる。また、共重合体中の繰り返し単位(a)の割合は、¹H-NMRにより、全ノルボルネン構造に由来する0.9～3.0 ppmのプロトンの吸収と5.4～6.9 ppmのC=C二重結合の炭素原子置換基のプロトンの吸収の比率から求めることができる。

【0030】本発明の環状オレフィン系共重合体には、2,6-ジ-*tert*-ブチル-4-メチルフェノール、4,4'-チオビス-(6-*tert*-ブチル-3-メチルフェノール)、1,1'-ビス(4-ヒドロキシフェニル)シクロヘキサン、2,2'-メチレンビス(4-エチル-6-*tert*-ブチルフェノール)、2,5-ジ-*tert*-ブチルヒドロキノン、ペンタエリスリチル-テトラキス[3-(3,5-ジ-*tert*-ブチル-4-ヒドロキシフェニル)プロピオネートなどのフェノール系、ヒドロキノン系酸化防止剤さらに、トリス(4-メトキシ-3,5-ジフェニル)ホスファイト、トリス(ノニルフェニル)ホスファイト、トリス(2,4-ジ-*tert*-ブチルフェニル)ホスファイト

ビス(2,6-ジ-*tert*-ブチル-4-メチルフェニル)ペンタエリスリチルジホスファイト

ビス(2,4-ジ-*tert*-ブチルフェニル)ペンタエリスリチルジホスファイトなどのリン系酸化防止剤を添加して、酸化安定性を向上させることができる。

【0031】本発明の環状オレフィン系共重合体には、ケイ素、アルミニウム、チタンおよびジルコニウムの群から選ばれた少なくとも1種の金属の酸化物、ならびに/またはアルコキシシラン化合物を加水分解・縮合して得られるシリコン酸化物(以下、これらを「金属酸化物」ともいう)を配合し、複合体としてもよい。

【0032】上記複合体としては、上記本発明の環状オレフィン系共重合体に、コロイダル状の、シリカ、アルミナ、チタニアなどの金属酸化物をアルコキシシラン基を有するアクリル酸エステル、またはメタクリル酸エステルで表面を変性したものと混合して共重合体中に金属酸化物がミクロに分散した架橋可能な複合体とすることもできる。

【0033】また、本発明の環状オレフィン系共重合体が、アルコキシシラン基を含有する場合は、上記金属酸

化物を表面変性することなく、共重合体中に金属酸化物がミクロに分散した架橋可能な複合体が得られる。

【0034】さらに、上記複合体としては、本発明の共重合体中に、Si、Al、Ti、Zrなどのアルコール塩、アリアル塩例えば、テトラメトキシシラン、テトラエトキシシラン、メチルトリメトキシシラン、メチルトリエトキシシラン、トリメトキシアルミニウム、トリエトキシアルミニウム、テトラエトキシチタン、テトラエトキシジルコンなどを溶液状態で混合後に、Sn、Ti、Zr、Y、Alなどの化合物、やHCl、HFなどの触媒を用いて、加水分解・重縮合する”ゾル-ゲル法”によっても架橋可能なハイブリッド複合体が得られる。共重合体中にこれら無機粒子が100nm以下、好ましくは10nm以下の粒径に分散されることにより、光学透明で耐熱性、寸法安定性が向上した複合体となる。

【0035】本発明の複合体において、上記金属酸化物の配合量は、本発明の環状オレフィン系共重合体100重量部に対し、通常、3～50重量部、好ましくは5～30重量部である。

【0036】本発明の環状オレフィン系共重合体(または複合体)は、押し出し機により、直接、フィルム、シート薄膜とすることもできるし、また炭化水素溶媒、ハロゲン化炭化水素溶媒、ケトン、エーテル、エステル、アミン、アミド、尿素など極性溶媒から選ばれた溶媒に共重合体(複合体)を溶解させ、キャストイング、蒸発工程を経て、光学透明なフィルムおよびシートにすることができる。また、これら溶媒に共重合体(複合体)を膨潤させたのち、押し出し機で溶媒を蒸発させながら、共重合体(複合体)をフィルム、シートに成形・加工することもできる。

【0037】本発明の環状オレフィン系共重合体、あるいは、その複合体は、光あるいは電子線などの活性エネルギー線により架橋でき、架橋を促進するために、芳香族化合物、芳香族カルボニル化合物、芳香族チオカルボニル化合物などの増感剤、有機および無機の過酸化物、スルフィド化合物、ジアゾ化合物、チオール化合物など少量添加することができる。架橋に用いられる光源としては、波長が250nm～450nmの光が用いられる。また、架橋条件は、温度が0～150℃で、時間が1～300分である。

【0038】本発明の環状オレフィン系共重合体、その複合体、これらの架橋体は、優れた光学透明性、耐熱性、接着・密着性を有するので、導光板、偏光フィルム、液晶パネル、位相差フィルム、透明導電性フィルム、OHPフィルム、光ディスク、光ファイバー、レンズなど光学部品(光学材料)、電子部品、さらに医療容器、容器などにも用いられる。

【0039】なお、本発明の環状オレフィン系共重合体(複合体)は、優れた光学透明性、耐熱性、接着性・密着性を有するため、従来、公知のノルボルネン系開環

(共)重合体の水素化物や付加(共)重合体(例えば、特開昭61-29260号公報、特開昭60-16870号公報、特開昭60-26024号公報、特開平2-51511号公報、特開平1-132625号公報、特開平1-132626号公報、特開平4-202404号公報、特開平4-63807号公報、特開平8-198919号公報、特表平9-508649号公報、特表平11-505880号公報、特開昭61-292601号公報など)を配合して熱可塑性重合体組成物となし、優れた耐熱性、光学特性(透明性、低屈折性、)、接着・密着性を付与することができる。

【0040】このような熱可塑性重合体組成物において、本発明の環状オレフィン系共重合体と他の(共)重合体との配合割合は、本発明の環状オレフィン系共重合体および他の(共)重合体の種類、両者の相溶性、組成物の使用目的に応じて、適宜選択されるが、優れた耐熱性を有する重合体組成物を得るためには、本発明の環状オレフィン系共重合体の割合が5~95重量%、好ましくは10~90重量%、さらに好ましくは、20~80重量%である。

【0041】このような熱可塑性重合体組成物は、押し出し機、バンパリーミキサー、ニーダー、ミキシングロールなどを用いる機械的混合や、溶媒に溶かして溶液ブレンドすることにより得られる。このような熱可塑性重合体組成物からも、本発明の環状オレフィン系共重合体の場合と同様に、フィルム、シートおよび薄膜を得ることができる。

【0042】

【実施例】以下、本発明を実施例によってさらに具体的に説明するが、本発明はこれらの実施例によって何ら制限を受けるものではない。なお、分子量、ガラス転移温度、屈折率、ガラス転移温度、線膨張係数、吸水率、接着・密着性は、下記の方法で測定した。

【0043】(1)重量平均分子量、数平均分子量：ウオターズ(WATERS)社製150C型ゲルパーミエーションクロマトグラフィー(GPC)装置で東ソー(株)製Hタイプカラムを用い、 α -ジクロロベンゼンを溶媒として、120℃で測定した。得られた分子量は、標準ポリスチレン換算値である。

(2)全光線透過率：ASTM-D1003に準拠し、厚さが100 μ mのフィルムにして、全光線透過率を測定した。

(3)Tan δ のピーク温度(ガラス転移温度)：動的粘弾性のTan δ (貯蔵弾性率E'と損失弾性率E''との比E''/E'=Tan δ)を測定し、その温度分散のピーク温度を共重合体のガラス転移温度とした。動的粘弾性の測定は、レオバイロンDDV-01FP(オリエンテック製)を用い、測定周波数が10Hz、昇温速度が4℃/分、加振モードが単一波形、加振振幅が2.5 μ mの条件で行った。

(4)線膨張係数：TMA(Thermal Mechanical Analysis)/SS6100(セイコーインスツルメント社製)を用いて、膜厚100 μ m、幅3mm、長さ10cmの試料を、チャック間距離10mmで固定し、室温から200℃程度まで一旦昇温して残留ひずみをとった後、室温から3℃/min.で昇温し、チャック間距離の伸びから線膨張係数を求めた。

(5)吸水率：23℃の水中に24時間浸漬させた後、浸漬前後の重量変化から吸水率を求めた。

10 (6)接着性・密着性：10cm×10cmの試験片にアルミニウムを蒸着し、この蒸着膜に対して、カッターにより、1mm×1mmの碁盤目が10個×10個、形成されるように、切り込みを入れ、セロハンテープによる剥離試験を行い、25ブロック中における剥離したブロックの数を測定した。

【0044】合成例1〔アクリル酸2-(5-ノルボルネニル)メチルの合成〕

500mlの耐圧ガラス容器中、窒素雰囲気下で5-ヒドロキシメチル-2-ノルボルネン 50g(0.403mol)とアクリル酸クロライド39.2ml(0.483mol)を塩化メチレン370mlに加え、さらにトリエチルアミン 84.3ml(0.605mol)を加え、25℃で3時間反応させた。その後、塩酸水溶液に注ぎ、炭酸ナトリウムで水相を中和して、有機相を分液ロートで分離した。重合防止剤であるペンタエリスリチルテトラキス〔3-(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネート〕を75mg添加して55℃、5mmHg下で蒸留した。アクリル酸2-(5-ノルボルネニル)メチルを47gを得た。(収率65%)

30 【0045】実施例1〔2-ノルボルネンとアクリル酸2-(5-ノルボルネニル)メチルの共重合体の合成〕300mlの耐圧ビンに窒素雰囲気下で水分5ppmのトルエンを100ml、2-ノルボルネン90mmol、アクリル酸2-(5-ノルボルネニル)メチル10mmolを仕込み、六フッ化アンチモン酸(HSbF₆)とオクタン酸ニッケル(Ni(oct)₂)を-30℃で予め、反応させた変性オクタン酸ニッケル(HSbF₆/Ni(oct)₂=1.2モル比)を0.04mg当量Ni、三フッ化硼素・エチルエーテル錯体0.36mmol、トリエチルアルミニウム0.40mmolの順に添加して、30℃で2時間、重合を行った。上記共重合体溶液に乳酸4mmolを含むイソプロパノール4mlを添加して、60℃、30分間反応させた後、水600mlに入れ、攪拌、静置分離して、共重合体溶液から脱触媒を行った。その後、共重合体溶液をイソプロパノール1,000mlに入れて凝固し、未反応単量体を除去し、共重合体を80℃、10時間乾燥して、白色粉末4.7gを得た。単量体の共重合体への転化率は46%であった。

【0046】共重合体の分析：

50 ・共重合体の組成

270MHz, ^1H -NMRで測定されるノルボルネン構造に由来する0.9~3.0ppmのプロトンピークとアクリル酸2-(5-ノルボルネニル)メチルに由来する $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-$ 置換基の CH_2 =プロトン5.4~6.5ppmからアクリル酸2-(5-ノルボルネニル)メチルに由来する構造単位の割合は3.2モル%であった。なお、ノルボルネン構造の開環重合により生成する $-\text{CH}=\text{CH}-$ 構造の5.0~5.3ppmのプロトンは観察されなかった。得られた共重合体の ^1H -NMRチャートを図1に示す。

・官能基の定性分析：赤外吸収スペクトルで $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-$ による $1,727\text{cm}^{-1}$ のエステル基の特性吸収と $\text{C}=\text{C}$ による $1,636\text{cm}^{-1}$ の特性吸収が観測された。得られた共重合体の赤外吸収スペクトルを図2に示す。

・分子量：GPCで測定される標準ポリスチレン換算の数平均分子量は108,000、重量平均分子量は233,000であった。

・ガラス転移温度： $\text{Tan}\delta$ の温度分散のピーク温度（ガラス転移温度）は 350°C であった。

・全光線透過率：厚さ $100\mu\text{m}$ のフィルムを用いて測定される全光線透過率は91%であった。

【0047】架橋処理

未架橋の厚さ $100\mu\text{m}$ のキャストフィルムはトルエンに 25°C で溶解した。このフィルムに500Wの高圧水銀ランプを用い熱線カットフィルターを介して 30°C で波長の主ピークが314、366、405、436nmの紫外線を30分照射すると、フィルムは 25°C のトルエンに不溶となった。

【0048】実施例2

アクリル酸2-(5-ノルボルネニル)メチルの代わりに、メタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}.]ドデセニル)メチルを用いる以外は、実施例1と同様に重合を行った。単量体の共重合体への転化率は82%であった。共重合体中のメタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}.]ドデセニル)メチルに由来する構造単位の割合は ^1H -NMR分析から、9.5mol%であった。GPCによる数平均分子量は113,000、重量平均分子量は226,000であった。実施例1と同様に紫外線の照射により、 25°C のトルエンに全く不溶なフィルムとなった。また、ベンゾイルパーオキシドを重合体100重量部当たり、0.5重量部添加して得たフィルムを9

0°C 、15分熱処理すると、 25°C 、トルエンに全く不溶なフィルムとなった。

【0049】実施例3

メタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}.]ドデセニル)メチル10mmolの代わりに、メタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}.]ドデセニル)メチル5mmol、5-トリエトキシシリル-2-ノルボルネン5mmolを用いる以外は、実施例1と同様に重合を行い、共重合体7.3gを得た。メタクリル酸3-(8-テトラシクロ[4.4.0.1^{2,5}.1^{7,10}.]ドデセニル)メチルに由来する構造単位の割合は ^1H -NMR分析より、4.8モル%であった。また、5-トリエトキシシリル-2-ノルボルネンに由来する構造単位の割合は、赤外分析で $1,389\text{cm}^{-1}$ の $-\text{Si}-\text{O}-\text{CH}_2\text{CH}_3$ 基の末端 CH_3 の吸収と $1,294\text{cm}^{-1}$ のノルボルネン骨格による $-\text{CH}-$ の吸収の相対比の検量線から求め、4.5モル%であった。この共重合体の数平均分子量は109,000、重量平均分子量は214,000であった。実施例1と同様に $100\mu\text{m}$ のフィルムを作成し、紫外線による架橋を行った。そのフィルムは 25°C のトルエンに全く不溶であった。このフィルムの全光線透過率は91%であった。アルミニウムの剥離テストでも剥離するブロックはなかった。

【0050】実施例4

メチル・エチルケトン400ml中でシリカ粒子（平均粒径12nm、比表面積 400m^2 、表面シラノール $5\mu\text{mol}/\text{m}^2$ ）、またはアルミナ粒子（平均粒径20nm、比表面積 150m^2 ）をそれぞれ100gに対して50gのメタクロイルオキシ（プロピル）トリメトキシシランを加え、さらに触媒として10mlの水に対して1.5gの無水マレイン酸を加えて、2時間、窒素下で環流した。この溶液からメチル・エチルケトンを減圧下で200mlを除去し、トルエン200mlを添加した。このようにして得た表面変性のコロイダルシリカまたはアルミナを実施例3の共重合体100重量に対して5重量部をトルエン溶液中で混合して、透明な複合化した溶液を得た。次に、その溶液をキャストして、約 $100\mu\text{m}$ のフィルムを得た。複合化したフィルムおよび光架橋したフィルムの特性値を表1に示す。

【0051】

【表1】

粒子の種類とフィ ルムの光架橋	全光線透過率 (%)	トルエンへの溶解	線膨張係数 (ppm/°C)
シリカ・未架橋	90	溶解	60
シリカ・架橋体	90	不溶	55
アルミナ・未架橋	90	溶解	62
アルミナ・架橋	90	不溶	57
なし、未架橋(実 施例3の共重合 体)	91	溶解	65

【0052】実施例5

実施例1において、アクリル酸2-(5-ノルボルネニル)メチルの代わりに、2-ヒドロキシエチルメタクリル酸エステルと2-メチル、5-ノルボルネン-2-カルボン酸のエステルを用いる以外、実施例1と同様に行った。重合体への転化率は、38%であった。重合体をトルエンで溶解し、アセトンで凝固して精製した後の赤外線吸収スペクトルでは、 $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-$ による $1,727\text{ cm}^{-1}$ の特性吸収が観測された。この構造に由来する構造単位の割合は、全繰返し単位中、2.8モル%であった。重合体の数平均分子量は39,000、重量平均分子量は66,000であった。実施例1と同様に、光による架橋が起こり、トルエンに不溶であった。

【0053】比較例1

実施例1にて、2-ノルボルネン90mmol、アクリル酸2-(5-ノルボルネニル)メチル10mmolの代わりに、2-ノルボルネン93mmol、5-エチリデン-2-ノルボルネン7mmol、を用い、溶媒としてシクロヘキサンを用いる以外、実施例1と同様に共重合反応を行い、*

共重合体7.6gを得た。GPCによる数平均分子量は98,000、重量平均分子量は198,000であった。実施例1と同様に $100\text{ }\mu\text{m}$ のフィルムを作成し、フィルムに紫外線を照射したが、シクロヘキサンに大部分溶解した。また、残った物も、糊状で原形をとどめなかった。また、実施例2と同様にベンゾイルパーオキシドを加えてフィルムを作成し加熱したが、シクロヘキサンに溶解した。さらに、アルミニウムの剥離テストを実施したところ、全て剥離し密着性が著しく弱かった。

20 【0054】

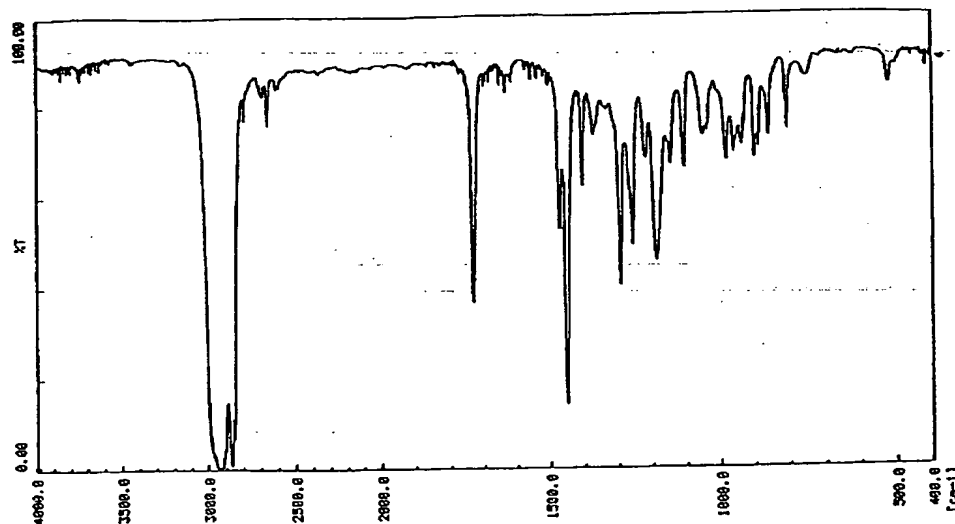
【発明の効果】本発明によれば、優れた耐熱性、透明性、耐薬品性、耐溶剤性および接着・密着性を付与することができる、架橋可能な環状オレフィン系共重合体、その複合体、さらにはこれらの架橋体を提供することができる。

【図面の簡単な説明】

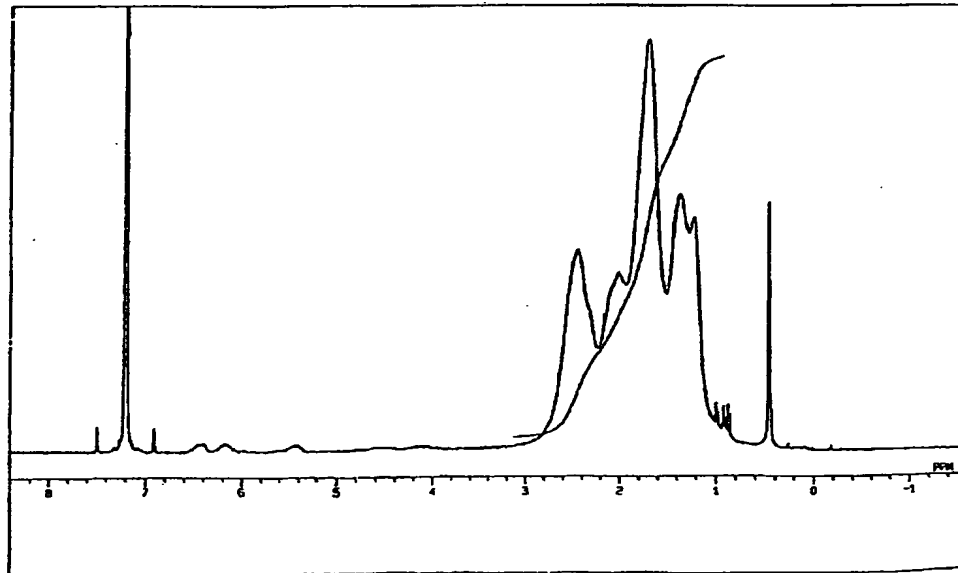
【図1】実施例1で得られた共重合体の $^1\text{H-NMR}$ のチャートである。

【図2】実施例1で得られた共重合体の赤外吸収スペクトルである。

【図2】



【図1】



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